that the elements of $\underset{\sim}{S2}^{-1}$ are simply related to the standard errors in the parameters (26). For the case of three parameters, the elements of the so-called covariance matrix are:*

$$
\begin{aligned}
\sigma_a^2 &= \underset{\sim}{S2}^{-1}_{aa}\,\sigma_o^2 & \sigma_{ab} &= \underset{\sim}{S2}^{-1}_{ab}\,\sigma_o^2 \\
\sigma_b^2 &= \underset{\sim}{S2}^{-1}_{bb}\,\sigma_o^2 & \sigma_{ac} &= \underset{\sim}{S2}^{-1}_{ac}\,\sigma_o^2 \\
\sigma_c^2 &= \underset{\sim}{S2}^{-1}_{cc}\,\sigma_o^2 & \sigma_{bc} &= \underset{\sim}{S2}^{-1}_{bc}\,\sigma_o^2
\end{aligned}
\qquad (2.2\text{-}17)
$$

The standard deviation, or standard error, in the parameter a is just σ_a, while the variance in a is σ_a^2. In many cases, estimates of the standard deviations of the parameters is as important as estimates of the parameters themselves. The former information, as Wentworth says, is impossible to obtain from a graphical solution and is one of its most limiting features (26b).

Knowledge of the covariance matrix also enables one to calculate the variance of any function of the parameters (26). Suppose we have a function

$$g = G(a,b,c) \quad . \qquad (2.2\text{-}18)$$

Then the variance of g is given by

$$
\begin{aligned}
\sigma_g^2 = {} & G_a^2\sigma_a^2 + G_b^2\sigma_b^2 + G_c^2\sigma_c^2 \\
& + 2G_aG_b\sigma_{ab} + 2G_aG_c\sigma_{ac} + 2G_bG_c\sigma_{bc}
\end{aligned}
\qquad (2.2\text{-}19)
$$

---

*In spite of appearances, eqs. 2.2-17 do not say that the uncertainties in the parameters depend on σ_o; this formulation merely neutralizes the effect of having allowed σ_o to be chosen arbitrarily.

where the usual notation for differentiation has been used; e.g.,

$$G_a = \left(\frac{\partial G}{\partial a}\right) .$$

The cross terms (covariance terms) in eq. 2.2-19 can be very important if the values taken by the parameters are highly interdependent. An example in which this happens to be the case is given in part D below.

C. Covergence

Criteria for convergence will depend on what one wishes to get out of the calculation. A simple minded approach, and that used in this work, is to iterate until no significant improvement is made. This could be done by comparing the change in S between iterations j and j+1 with a suitably chosen convergence parameter to decide whether to perform iteration j+2. However, we can write

$$S(j+1) - S(j) \cong - S_a \Delta a - S_b \Delta b - S_c \Delta c$$

by dropping the second-order terms in eq. 2.2-4. Thus, we can instead make the comparison at the end of iteration j.

It may, of course, happen that the iteration diverges. In such cases, S(j+1) - S(j) as obtained above will become positive. The computer can be directed to terminate the current set of iterations if this happens. We should note, however, that in difficult problems, such as the fit to the R1 and R2 product-ratio data, a temporary increase in S may occasionally be necessary to make ultimately beneficial adjustments in the parameters, so one would want S(j+1) - S(j) to be larger than a predetermined quantity before allowing the termination of the iteration.

In fitting the R1 and R2 product-ratio data, we have included only eight of the most sensitive parameters in the iterative optimization (see p. 207). Unfortunately, stability problems, as partially explained in part D below, were sufficiently severe that it was not in general possible to begin by optimizing all eight simultaneously. We therefore worked with smaller sets of parameters until the fit was fairly refined. This was done by preparing a series of control cards, each specifying a set of parameters to be optimized, the maximum number of iterations to be done on that set (typically five) and a convergence parameter. When we had $0 > S(j+1) - S(j) >$ convergence parameter, the computer was instructed to discontinue the current set of iterations and read in the next control card, if any. But if S(j+1) - S(j) became 'large' and positive, the run was aborted. This procedure allowed us to gradually work up to iterations on the full parameter set without committing ourselves to an unnecessarily lengthy and time-consuming series of iterations.

D. An Example Concerning Parameterization

Perhaps it will be helpful to go through an example illustrating the implementation of the least-squares formalism. The example chosen will also enable us to make a point of potential interest concerning the parameterization of the Arrhenius equation.

Suppose we have obtained a series of N measurements of a rate constant k at various temperatures which we wish to fit to the Arrhenius equation:

$$k_i = ae^{-b/RT_i}, \quad i = 1, N \tag{2.2-20}$$

If we take a^o and b^o as initial approximations to the parameters, we can write*

$$F_i^o \equiv k_i - a^o e^{-b^o/RT_i} \quad .$$

The derivatives with respect to the parameters are:

$$F_{a_i} = -e^{-b^o/RT_i}; \qquad F_{b_i} = \frac{a^o}{RT_i} e^{-b^o/RT_i};$$

and those with respect to the observables are:

$$F_{k_i} = 1; \qquad F_{T_i} = -\frac{a^o b^o}{RT_i^2} e^{-b^o/RT_i} \quad .$$

Let us further suppose that the measurements of k_i are uncertain by ± 10 percent and that our constant temperature bath is good to ± 0.1°. If we then choose $\sigma_o = 0.1$, we have that

$$L_i = k_i^2 + (F_{T_i})^2 \quad .$$

---

*We could of course have taken F_i^o to be the negative of that given here.

These quantities may then be assembled according to the recipe of eqs. 2.2-12.

As a 2 X 2 matrix is trivial to invert, let's carry the solution through symbolically. Using the notation of part B above, the inverse matrix is

$$\underset{\sim}{S2}^{-1} = \begin{pmatrix} \underset{\sim}{S2}_{bb}/\Delta & -\underset{\sim}{S2}_{ba}/\Delta \\ -\underset{\sim}{S2}_{ab}/\Delta & \underset{\sim}{S2}_{aa}/\Delta \end{pmatrix} ,$$

where

$$\Delta = (\underset{\sim}{S2}_{aa})\,(\underset{\sim}{S2}_{bb}) - (\underset{\sim}{S2}_{ab})^{2} \quad . \tag{2.2-21}$$

(Remember that by symmetry $\underset{\sim}{S2}_{ab} = \underset{\sim}{S2}_{ba}$). The correction quantities are then found to be:

$$\begin{aligned} \Delta a &= \frac{(\underset{\sim}{S2}_{bb})(\underset{\sim}{S1}_{a}) - (\underset{\sim}{S2}_{ab})(\underset{\sim}{S1}_{b})}{\Delta} \\ \Delta b &= \frac{(\underset{\sim}{S2}_{aa})(\underset{\sim}{S1}_{b}) - (\underset{\sim}{S2}_{ab})(\underset{\sim}{S1}_{a})}{\Delta} \end{aligned} \tag{2.2-22}$$

The interesting point about this result is that the parameters in the Arrhenius equation are such that

$$(\underset{\sim}{S2}_{ab})^{2} \approx (\underset{\sim}{S2}_{aa})(\underset{\sim}{S2}_{bb}) \quad .$$

That is, the quantity Δ very nearly vanishes.

The near vanishing of Δ arises from the strong coupling between the two parameters of the Arrhenius equation. The existence of this coupling means that in trying to improve a given set of parameters, it simply will not do to optimize the fit with respect to one, while holding the other constant, then to optimize the second, and so on; one must adjust both parameters simultaneously by making properly correlated changes.

To see the correctness of this reasoning, suppose that the parameters are uncorrelated--that $(\underset{\sim}{S2}_{aa})(\underset{\sim}{S2}_{bb}) >> (\underset{\sim}{S2}_{ab})^2$. Eqs. 2.2-22 would then simplify to

$$\Delta a = \underset{\sim}{S1}_{a} / \underset{\sim}{S2}_{aa} \; ;$$

$$\Delta b = \underset{\sim}{S1}_{b} / \underset{\sim}{S2}_{bb} \; ;$$

and it would be possible to optimize the parameters sequentially.

The reason this subject interests us is that, in problems of any size, strong correlation between various parameters will lead to near cancellation of terms involved in the matrix inversion and thus will aggravate any problems of numerical stability. As a result, a series of iterations which is apparently converging smoothly may simply 'jump the tracks' and become hopelessly lost. Each of the arabic-letter parameters for the product ratios R1 and R2 (see eqs. 2.1-4, p. 203) can be described in terms of a composite activation energy and a composite preexponential factor. When such a description was used in the early stages of the mechanistic calculations, convergence was at best highly erratic. Fortunately, a simple way was found to rewrite the Arrhenius equation with 'decoupled' parameters, whereupon smooth convergence was generally obtained (see part C above). The computationally preferred form of the Arrhenius equation for a rate constant k is

$$k = a' e^{-b(1/RT - 1/R\overline{T})} , \qquad (2.2\text{-}23)$$

where $\overline{T}$ is a value of T near the middle of the range of temperatures investigated experimentally, a' is the least-squares estimate of k at $T = \overline{T}$, and b is again the Arrhenius activation energy.

It should be noted that the least-squares treatment of the unmodified Arrhenius equation (eq. 2. 2-20) outlined in this subsection is perfectly adequate for that simple two-parameter problem. Thesis equations 1. 7-5 and 1. 8-11 were determined in that way. For the many-parameter problem of the present Section, however, the parameterization employed in eq. 2. 2-23 had to be used.

We can show very simply that the new parameters are at most weakly coupled with the aid of Fig. 19, in which hypothetical rate-constant data are plotted against 1/T according to the well-known logarithmic form of the Arrhenius equation. The parameter b is of course related to the slope of the best straight line through the data, while a is related to the left-intercept.

The reader at this point is to play the role of a digital computer in attempting to correct an initial approximation (e. g. , the straight line of Fig. 19) by adjusting one parameter at a time. The test is then this: if an initial, rather poor, approximation can be substantially improved in this manner, the parameters are only weakly coupled; otherwise, strong coupling is indicated.

Let us begin with the Arrhenius equation as it is usually written. The reader, presumably employing a clear plastic rule, is directed to adjust the initial line so as to reduce the sum of the squares of the deviations by changing the slope while keeping the intercept constant, or vice-versa.

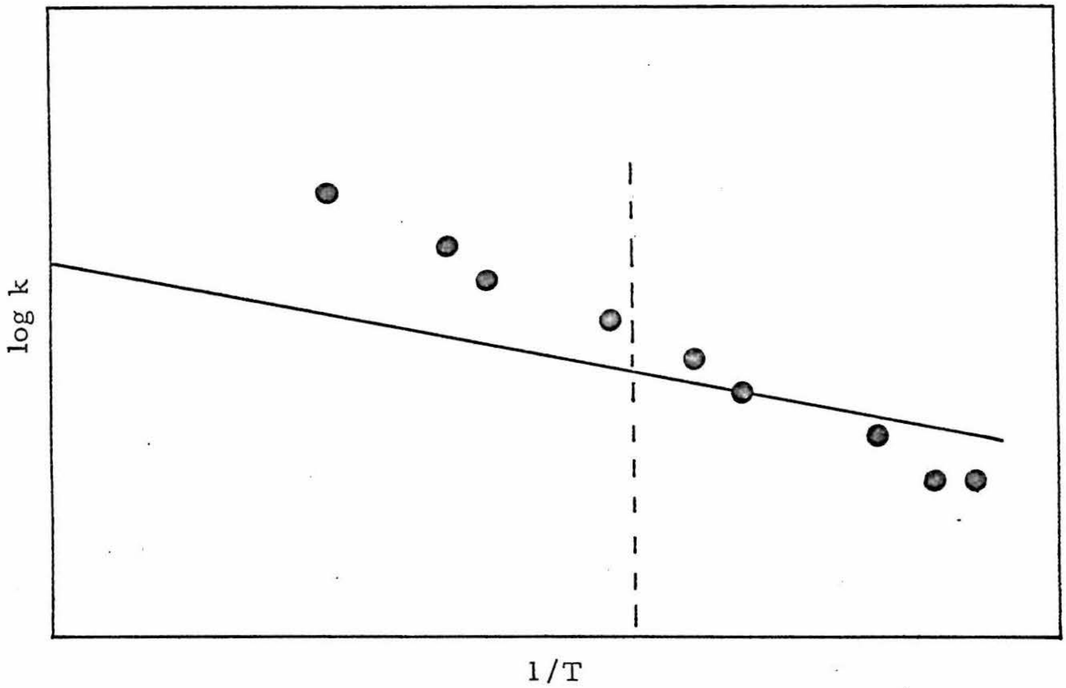

Figure 19. Hypothetical rate data illustrating correlation of parameters in the Arrhenius equation.

The reader will quickly notice that whether the slope or the intercept is varied first, the fit is improved at least to the extent that the new line intersects the data near the center of the temperature range. On attempting to adjust the other parameter, however, things get a little sticky; no clear improvement can be made.

A more complicated operation consisting of a simultaneously varying slope and left-intercept is clearly needed.

Let's try now with the modified Arrhenius equation, eq. 2.2-23. The parameters are now effectively the slope and the intercept of the straight line with the vertical dotted line (which marks the approximate center of the temperature range). Note that the solid line moves in the same way in varying this intercept as it did in varying the left-intercept. On varying the slope, however, we now pivot about the intercept with the dotted line instead of about the left-intercept; and this makes all the difference in the world. Optimizing the new parameters sequentially leads to smooth convergence to a line which fits the data well. That is, the new parameters are substantially uncorrelated.

Accordingly, arabic-letter parameters arising in the mechanistic description of this Section have been described according to eq. 2.2-23 rather than eq. 2.2-20, where $\overline{T}$ has uniformly been taken to be 100° C.

The fact that the normal Arrhenius equation parameters are strongly correlated leads to a result well known to chemical kineticists, namely, that the standard deviations in the preexponential factor and the activation energy one estimates from a given set of data are quite large compared to the uncertainty in the rate measurements themselves. This again reflects the near vanishing of the quantity Δ of eq. 2.2-21 and the corresponding importance of the covariance term σ_{ab} of eqs. 2.2-17 in expressions based on eq. 2.2-19.

3. Application of the Least-Squares Formalism to Thermal Decomposition of the Peresters in 1,4-Cyclohexadiene

The formalism of subsection 2 dealt with a situation in which N observations on a single product ratio were to be fit to a theoretical expression. In this work, we are interested in simultaneously fitting N observations on each of two product ratios, R1 ≡ % yield **5**/% yield **10** and R2 ≡ % yield **6**/% yield **5**.

Therefore we generalize eq. 2.2-16 to

$$S = \sum_{i=1}^{N} \left\{ \frac{(F1_i^{o})^2}{L1_i} + \frac{(F2_i^{o})^2}{L2_i} \right\} \tag{2.3-1}$$

where $L1_i$ and $L2_i$ are the weighting factors for the various observations (see below) and

$$\begin{aligned} F1_i^{o} &= R1_i^{calc} - R1_1^{obs} \ ; \\ F2_i^{o} &= R2_i^{calc} - R2_i^{obs} \ . \end{aligned} \tag{2.3-2}$$

Each summation in eqs. 2.2-12 (the normal equations) will contain two components, one for R1 and the other for R2.

Evaluation of the necessary derivatives of $F1^{o}$ and $F2^{o}$ with respect to the parameters consists of working out expressions for the derivatives of $R1^{calc}$ and $R2^{calc}$. As was previously noted, we shall include in the optimization procedure only the arabic-letter parameters E--I of eqs. 2.1-4. Each of these, however, requires two parameters for description via a modified Arrhenius equation (eq. 2.2-23). Thus, if E2 is the activation energy for the composite parameter E, we need an expression for $(\partial R1^{calc}/\partial E2)$. As E2 does not appear explicitly in any of our mechanistic equations, we can write

$$\begin{aligned}\left(\frac{\partial R1^{calc}}{\partial E2}\right) &= \left(\frac{\partial R1^{calc}}{\partial E}\right)\left(\frac{\partial E}{\partial E2}\right)\\ &= \left\{\left(\frac{\partial Y5}{\partial E}\right)/Y10 - R1^{calc}\left(\frac{\partial Y10}{\partial E}\right)/Y10\right\}\left(\frac{\partial E}{\partial E2}\right)\ ,\end{aligned} \tag{2. 3-3}$$

where Y5 represents the theoretical expression for % yield of ring-opened hydrocarbon $\underset{\frown}{5}$ (i. e., eq. 2. 1-1).

Thus, we need to work out expressions for the derivatives of eqs. 2. 1-1—2. 1-3 with respect to the arabic-letter parameters, E, F, G, H, and I. Because of the complexity of those equations, this task is not trivial. The principal complication arises from the appearance of the variables W and X in the product-yield expressions. Thus, the variation of an arabic-letter parameter will cause changes in the calculated product yields not only in accordance with the incorporation of a parameter into the product yield expressions, but also through the effect of changes in that parameter on the values of the variables W and X.

For example, the expression for $(\partial Y5/\partial E)$ involves the following terms:

$$\begin{aligned}\left(\frac{\partial Y5}{\partial E}\right)_{O,P'} &= \left(\frac{\partial Y5}{\partial E}\right)_{O,P',V} + \left(\frac{\partial Y5}{\partial W}\right)_{O,P,V'}\left(\frac{\partial W}{\partial E}\right)_{O,P',V}\\ &\quad + \left(\frac{\partial Y5}{\partial X}\right)_{O,P,V'}\left(\frac{\partial X}{\partial E}\right)_{O,P',V}\end{aligned} \tag{2. 3-4}$$

The subscripts indicate quantities held constant in the partial differentiations, according to the following pattern: the subscript O to each partial means that all the observables (the reaction temperature, the perester concentration, the 1, 4-cyclohexadiene concentration) are held constant; P refers to the parameters, P' meaning that all parameters are held constant except the one by which differentiation is indicated; similarly, V refers to the variables W and X. Thus, the $(\partial Y5/\partial E)$ on the left-hand side is the quantity desired for substitution into eq. 2. 3-3, whereas that on the right-hand side is obtained from eq. 2. 1-1 on the assumption that W and X are independent of E; its value is $100\alpha \int_0^1 W^*(ZH)\,dz$.

The terms $(\partial Y5/\partial W)$ and $(\partial Y5/\partial X)$ are similarly obtained by differentiation of eq. 2. 1-1. More difficult to come by are the partials $(\partial W/\partial E)$ and $(\partial X/\partial E)$. As we do not have explicit expressions for W and X we must employ implicit differentiation. For convenience, let us call eq. 2. 1-9 the W equation, or WEQ, and eq. 2. 1-10, XEQ. Differentiating WEQ by E we again get three terms:

$$\left(\frac{\partial WEQ}{\partial E}\right)_{O,P'} = \left(\frac{\partial WEQ}{\partial E}\right)_{O,P',V} + \left(\frac{\partial WEQ}{\partial W}\right)_{O,P,V'}\left(\frac{\partial W}{\partial E}\right)_{O,P',V} + \left(\frac{\partial WEQ}{\partial X}\right)_{O,P,V'}\left(\frac{\partial X}{\partial E}\right)_{O,P',V} = 0 \qquad (2.\,3\text{-}5)$$

This equation is similar in form to eq. 2. 3-4 for $(\partial Y5/\partial E)$, except that we know the sum of the terms to be zero because we originally had WEQ = 0. The partials $(\partial WEQ/\partial E)_{O,P',V}$, $(\partial WEQ/\partial W)$ and $(\partial WEQ/\partial X)$ simply come out to be numbers when current values of the various kinds of quantities are plugged into the derived expressions; $(\partial W/\partial E)$ and $(\partial X/\partial E)$ are unknown. Differentiating XEQ by E gives a second equation which is also linear in the unknowns $(\partial W/\partial E)$ and $(\partial X/\partial E)$. Combination of the two equations then yields the values of the unknowns which are to be substituted into eq. 2.3-4 and a host of sister equations which concern other product yields and other parameters.

We also require deviatives of $F1^{o}$ and $F2^{o}$ with respect to the observables in order to form the weighting factors L1 and L2. By analogy to eq. 2.2-14, we have

$$L1_i = (1/\sigma_o)^2 \left\{ \left(\sigma_{R1_i^{obs}}\right)^2 + \left(\frac{\partial R1_i^{calc}}{\partial ZH}\right)^2 \sigma_{ZH_i}^{\;2} + \left(\frac{\partial R1_i^{calc}}{\partial T}\right)^2 \sigma_{T_i}^{\;2} \right\} , \qquad (2.3\text{-}6)$$

and similarly for $L2_i$. As noted previously, σ_o is to be chosen purely for numerical convenience; here we have taken it to be 0.05.

We have assumed that $\sigma_{R1_i^{obs}}$ and $\sigma_{R2_i^{obs}}$ are given by equations such as eq. 2.3-7,

$$\sigma_{R1_i^{obs}} = s_i(R1_i^{obs}) \qquad (2.3\text{-}7)$$

where s_i expresses the relative uncertainty in $R1_i^{obs}$. For the R1 ratios, we have taken $s_i = 0.05$.

For the R2 ratios, however, a range of s_i values has been adopted as appropriate to varying conditions of vpc resolution. For runs in which the perester employed is the ring-closed 2, $R2^{obs}$ is not greatly different from unity. The result is that relative areas of the neighboring peaks due to ring-opened 5 and ring-closed 6 (the latter at 1.25 x the retention time of the former) could be measured with considerably better precision than the well-separated peaks due to 5 and 10 (relative retention time ~ 2.4) that determine the R1 ratios; for these runs, s_i was taken to be 0.03. On the other hand, the $R2^{obs}$ starting from ring-opened perester 1 are typically on the order of 0.02. An attenuation change following the appearance of the peak due to 5 was therefore required to give measureable peak heights for 6. The result, for the data of Table 1, was that triangulation had to be used rather than electronic integration. Even this was compromised by uncertainty as to the location of the base line caused by the presence of a peak attributed to the diphenylbutadiene 13 immediately following the peak due to 6. Thus, for these runs we have taken $s_i = 0.075$. In contrast, the use of retention times for 5 and 6 for the $R2^{obs}$ of Tables 4 and 5 about an order of magnitude longer than those employed in Table 1 (~ 40 min vs. 4 min) allowed unambiguous determination of the base line for computation of areas due to 6: for these runs, we have taken $s_i = 0.05$.

Uncertainty in 1,4-cyclohexadiene concentrations also can cause calculated product ratios to deviate from the observed quantities. This source of error is taken into account through the second term in braces in eq. 2.3-6, where we have taken*

$$\sigma_{ZH_i} = 0.05 + 0.1(P)_{o_i} \text{ (molar)} \quad . \qquad (2.3\text{-}8)$$

The motivation for the assumed dependence on the initial perester concentrations is that lack of precise knowledge of the quantity of 1,4-cyclohexadiene consumed in the reaction will make the instantaneous ZH concentrations employed in the mechanistic equations uncertain over and above the uncertainty incurred in making up the reaction mixtures.

Reaction temperatures were assumed to be good to ± 1° (i.e., $\sigma_{T_i} = 1.0$) except for runs at 70° for perester 2 (Table 2) and 150° for perester 1 (Table 1) where warm-up times of ~1 min are comparable to reaction half-lives calculated from activation parameters for perester decomposition discussed below (p. 235). In the latter cases, we have taken $\sigma_{T_i} = 3$. However, the actual calculations showed that in no case did the assumed uncertainty in the reaction temperature play a significant role.

For completeness, eq. 2.3-6 should also include a term arising from uncertainty in the initial perester concentration. The omission was originally an oversight. Fortunately, this is not a serious matter;

---

*Because thermal expansion of reaction mixtures has been taken into account approximately, true initial 1,4-cyclohexadiene concentrations may differ from those listed in Tables 1, 2, 4, 5, and 6 by considerably more than 0.05 M. But this would be a systematic error which would simply serve to slightly distort the calculated value for the parameter E, which multiplies the cyclohexadiene concentrations; this circumstance should not be allowed to play havoc with the relative weights of the various product-ratio observations.

if the initial perester concentrations are assumed to be good to at least ± 10%, one can easily show that the $L2_i$ would be increased by not more than 10% for initial conditions investigated in this work, and that the correction to the $L1_i$ would be infinitesimal.

According to eq. 2.3-6, we also need expressions such as $(\partial R1^{calc}/\partial ZH)$ and $(\partial R1^{calc}/\partial T)$. Derivatives with respect to the cyclohexadiene concentration were obtained by the approach outlined in eqs. 2.3-4 and 2.3-5. The reaction temperature comes into our mechanistic equations implicitly through the arabic-letter parameters A–I and through k_o, the rate constant for perester decomposition. We already have available the derivatives of $R1^{calc}$ and $R2^{calc}$ with respect to the parameters E–I. This information, plus derivatives with respect to k_o, allows us to assemble $(\partial R1_i^{calc}/\partial T)$ and $(\partial R2_i^{calc}/\partial T)$; the product ratios are sufficiently insensitive to the parameters A–D that the dependence on these quantities need not be included.

In view of the complexity of the starting eqs. 2.1-1 through 2.1-10, working out expressions for all the required partial derivatives would have been a prodigious undertaking. For example, the quantity of interest is in one case buried in the denominator of one component of a term to the one-half power which is in the denominator of a term which is in the denominator of the main expression. Fortunately, however, there is available a computer system known as FORMAC (for formula manipulation compiler) which is capable of performing a useful variety of operations on symbolic expressions (102). In this work, FORMAC's differentiation capability was employed to generate expressions for the desired partial derivatives.

The procedure essentially involved writing a control program containing instructions to read in expressions from punched cards, to differentiate those expressions with respect to a given variable, and to print out and punch out the results. The expressions read in were the integrands of eqs. 2.1-1—2.1-3, eqs. 2.1-5 and 2.1-6 for S and T, and the W and X equations, eqs. 2.1-9 and 2.1-10. Our job was then essentially reduced to seeing that numerical values for the component expressions were properly combined, as in eqs. 3.2-3—3.2-5, in the main product-ratio program.

Unfortunately, FORMAC puts out results in a form which seems calculated to require the maximum execution time on the computer. For example, A/B comes out as $A*B^{-1}$, and the latter takes ~ 20 times as long to execute on the IBM 7094. Therefore, it was necessary to recode the expressions generated by FORMAC, during which frequently recurring subexpressions were given symbolic names so as to be calculated only once (per integration mesh point, per data point, per iteration). The recoding reduced the execution time from ~ 25 sec to 4–5 sec per iteration.

The necessity of recoding the FORMAC-generated expressions is a minor objection, however; certainly the availability of FORMAC was the determining factor in the decision to pursue the mechanistic description to the present level of sophistication.

4. Results and Conclusions of the Least-Squares Optimization

A. Selection of Activation Parameters for Perester Decomposition

We now must settle on values to be used for the rate constants for thermal decomposition of the peresters 1 and 2. As noted previously, only a single rate-constant value is available for each of the peresters. Therefore, we shall have to make use of the relationship of structure to activation parameters for perester decomposition discussed in subsection 3 of Section One.

In a careful infrared study, Howden found the rate constant for thermal decomposition of ring-opened perester 1 in chlorobenzene at 109.7° to be 7.71×10^{-5} $\sec^{-1}$. This result is the average of two determinations which differed by only 2%. The solutions were 0.1 M in perester and 0.25 M in iodine (added to prevent radical-induced decomposition). Although first-order kinetics was observed in each of the two runs for somewhat less than two half-lives (after which the rate of decomposition substantially increased), the initial first-order behavior appears to reflect simple thermal decomposition of the perester.

The half-life of 150 min computed from Howden's rate constant agrees well with those of other primary peresters quoted in Table 13, p. 51. It seems reasonable to assume that the enthalpy of activation for normal homolytic decomposition of 1 is similar to the values of 35.3 and 35.0 kcal/mole quoted in Table 13 for two long-chain primary peresters. However, we must remember that k_o for perester 1 also includes the rate of molecule-induced decomposition (Section One, subsection 6). From reported enthalpies of activation for Koenig and Martin's *ortho*-diphenylvinyl perbenzoate, 26.4 kcal/mole, and for *t*-butyl perbenzoate itself, 34.2 kcal/mole, we expect the rate of molecule-induced decomposition of **1** to increase less rapidly with increasing temperature than the rate of normal homolytic decomposition. The difference of ~8 kcal/mole in the enthalpies of activation of the model perbenzoates would suggest, if applicable here, that the fraction of molecule-induced decomposition at 150° should be only about one-third that at 99°. This prediction appears to be too extreme to be compatible with the scattered (though admittedly not very accurate) determinations of the yield of the lactone **23** reported in Table 1, p. 28.

We have therefore assumed enthalpies of activation of 35.2 kcal/mole for normal homolytic decomposition of **1** and 31.2 kcal/mole for molecule-induced decomposition. A compromise value of 34.3 kcal/mole is then dictated by the relative importance of the two kinds of processes in the temperature range of interest and an entropy of activation of 11.70 e.u. is required to fit the half-life of 150 min at 110°. These values have been employed in the calculations reported below.

For the ring-closed perester **2**, only a rough rate determination is available. The absorbance data plotted in Fig. 20 were obtained on a cumene solution which was initially 0.10 M in **2** and which was open to the air and was maintained at approximately 23° C in a thermostated room. The absorbance measurements were obtained by intermittantly scanning a region containing the carbonyl stretching band of **2** using a Perkin-Elmer Infracord Model 237.

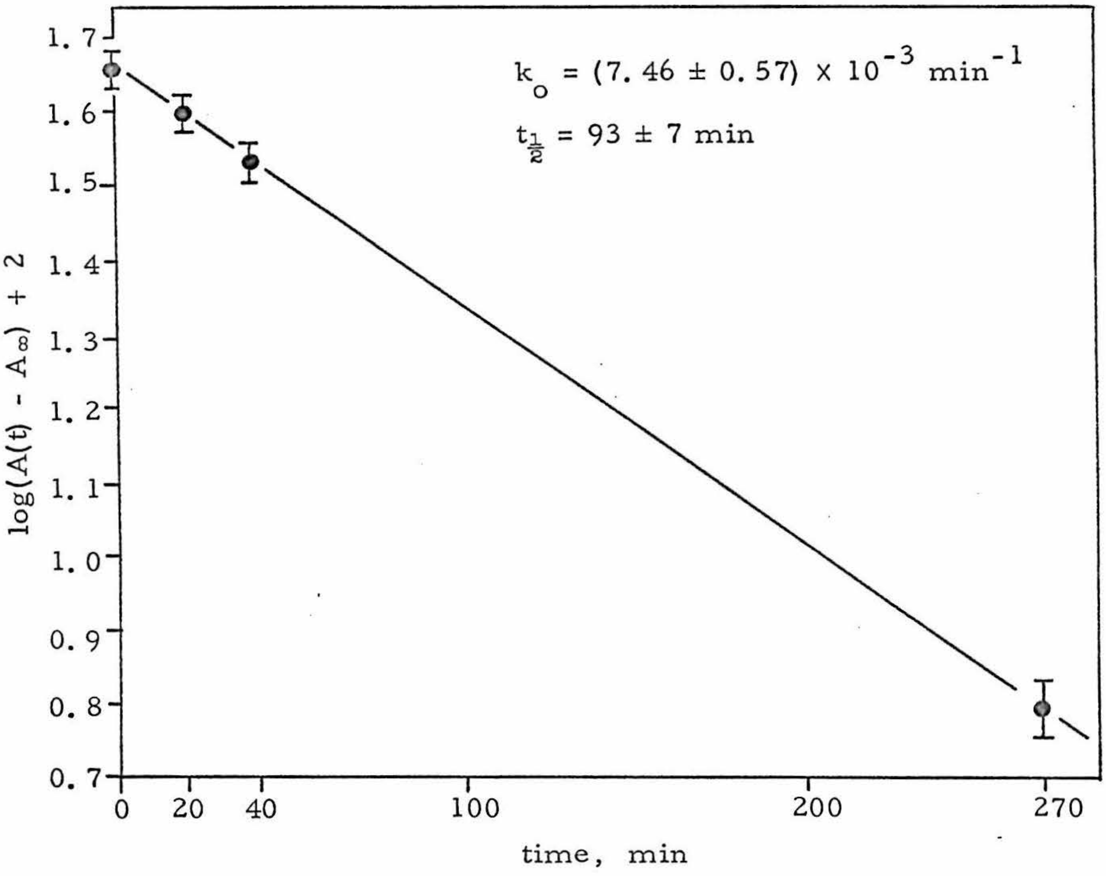

Figure 20. Decomposition of t-butyl diphenylcyclopropylacetate (0.10 M) in cumene at 23 ± 1° in the presence of air; A_∞, obtained for 18 hr reaction time, was 0.024.

Veteran observers will recognize that the conditions described here are more appropriate for an order-of-magnitude estimation than for the careful determination of a rate constant needed for quantitative analysis of experimental data. Indeed, the purpose of the rate measurement was simply to enable us to estimate reaction times corresponding to approximately 10 perester-decomposition half-lives for use in the degassed thermal decompositions reported in Tables 2 and 6.

A least-squares treatment gives $k_o = 1.24 \times 10^{-4}\ \mathrm{sec}^{-1}$ and $t_{\frac{1}{2}} = 93 \pm 7$ min at 23°. The estimated uncertainty in the half-life reflects assumed uncertainties of 5–10% in the absorbance data, as indicated by error bars in Fig. 20. For comparison, extrapolated half-lives at 23° are 90 min for *t*-butyl triphenylperacetate and 4100 min for *t*-butyl diphenylperacetate. Activation parameters for these peresters are 24.1 and 25.0 kcal/mole, respectively (see Table 13). Clearly, the rate of decomposition of **2** is very similar to that of *t*-butyl triphenylperacetate. If we take the enthalpy of activation for decomposition of **2** to be 24.5 kcal/mole, the half-life of 93 min at 23° requires an entropy of activation of 6.38 e.u.

Actually, we are not rigorously wedded to the half-life estimate of 93 min, for the uncertainty of ± 7 min which comes out of the least-squares treatment is only part of the story. For example, the true reaction temperature might have been one degree higher or lower than was read off the wall thermostat; the associated error in the half-life at 23° would be ± 15%. Moreover, solvent effects on the rate of decomposition are conceivable, though of uncertain magnitude. Finally, the spacing of the absorbance measurements in time is unfortunate. It is not unusual to have first-order kinetic plots depart from linearity well before three half-lives have been reached; Howden's rate determinations on perester **1** constitute one such example. Thus, it would be dangerous to rely heavily on the measurement at 270 min. On repetition of the least-squares analysis using only the first three points, a half-life of 115 ± 43 min was found. We take this to mean that we are not likely to be off by orders of magnitude in perester-decomposition half-life, but that the 93 ± 7 min may be a bit too restrictive.

A possible experimental objection, the presence of air during the decomposition, is probably unimportant. Oxygen would be expected to influence the disposition of radical intermediates, but not the rate of their formation in the absence of radical-chain processes.

As a result of these considerations, a preliminary series of least-squares calculations was carried out employing a range of decomposition half-lives for **2** at 23°. The average deviations between calculated and observed product ratios R1 and R2 were found to be 7.4%, 7.0%, 6.9%, and 7.2% for assumed decomposition half-lives of 75, 93, 112, and 137 min, respectively.* Thus, (a) the quality of the fit to the ratio data is reasonably insensitive to the half-life of **2** at 23° and (b) the value which optimizes the preliminary fit is not very different from that determined experimentally.

Especially encouraging, as we shall see in detail below, is that the reaction mechanism is able to account for the observation that the ratios **6**:**5** are typically 0.5 starting from **2** (Table 2), but only about 0.02 starting from **1** (Table 1) and for a variation of a factor of 300 between maximum and minimum values. Thus, the basically satisfactory character of the fit frees us from any real worries as to the basic adequacy of the assumed reaction mechanism. Our main concern will therefore be to see whether the product ratios can universally be correlated within reasonable experimental error or whether the presence of systematic deviations between calculated and observed product ratios points to areas in which the reaction mechanism is not fully

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*The quantity cited here is AVDEV, eq. 2.4-3, p. 248.

satisfactory. Therefore, a half-life at 23° of 112 min has been adopted so that deviations between calculated and observed ratios need not be artificially inflated by simple application of an admittedly crude rate measurement for 2. Accordingly, values of 24.5 kcal/mole for the enthalpy of activation, and 6.00 e.u. for the entropy of activation, for decomposition of 2 have been used in the calculations reported below.

B. Selection of Values for Non-Iteratively-Improved Parameters

We have, for a number of reasons, elected to determine only certain of the parameters appearing in the mechanistic equations via least-squares optimization of the fit to the product-ratio data. The purpose of this section is to explain the values adopted for the remaining, non-iteratively improved parameters.

(1). The parameter $A \equiv \omega/\alpha$ gives the ratio of decomposition events for ring-opened perester 1 which proceed via molecule-induced decomposition to those which involve normal homolytic decomposition but which bypass cage reactions to give a kinetically-free radical pair consisting of a hydrocarbon radical (either ring-opened 3 or ring-closed 4) and a t-butoxy radical. We have taken the value of A to be 0.25 at 100° and have assumed a composite activation energy of -4 kcal/mole. These values are intended to roughly account for the average yield of the lactone 23 of approximately 15% for determinations reported in Table 1 and for the expected lesser importance of molecule-induced decomposition at higher temperatures (p. 236).

Of course, whenever the starting perester is ring-closed 2, A is set to zero.

Preliminary calculations indicated that the fit to the product-ratio data would be improved by choosing A to be smaller than has been done. But it would be improper to allow A to be so chosen because a substantial value is required to account for the formation of the lactone 23, something the product-ratio program knows nothing about.

Incidentally, the values of α employed in all of the calculations are recorded in Table 17, p. 298. These values were chosen with reference to (a) the ratios ω/α, (b) smoothed yields of cage-reaction products which determine the parameter β, and (c) the normalization $\alpha + \beta + \omega = 1$.

(2). The parameter $B \equiv k_5k_d/k_6k_3^{\frac{1}{2}}$ has been assigned a composite preexponential factor of unity and a composite activation energy of 12 kcal/mole in most of the calculations reported below. As noted previously, B controls the competition between hydrogen abstraction by lactonyl radicals (22) from 1,4-cyclohexadiene (k_5) and from cyclohexadienyl radical (k_6). This parameterization, which forces the hydrogen abstraction to occur essentially totally from cyclohexadienyl radical, seemed quite reasonable when we mistakenly had $B \equiv k_5/k_6$,

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[*] Yields of B quoted in Table 2 apparently represent the combined yields of the cage combination product (ring-closed ether 15), the cage disproportionation product (the methylenecyclopropane 16), and (isomeric) tetrahydronaphthalenes (see pp. 71, 80). Values of β for these reactions were obtained by subtracting calculated yields of tetrahydronaphthalene (see Table 17) from observed yields of B.

but now appears to be indefensible. We shall therefore explore, under heading F, p. 268, the consequences of adopting reasonable values of B.

(3). The parameter $C \equiv k_7 k_d / k_b^{\odot} k_3$ controls the extent of reaction of ring-closed radical 4 with ring-cyclized radical 9. One can argue, from the manner in which the four radical-radical rate constants are arranged in the definition, that the expected value of C should be unity. For example, if reaction of ring-closed 4 with ring-cyclized 9 (k_7) is slower than reaction of 4 with cyclohexadienyl radical ($k_b^{\odot}$), one might also expect that reaction of 9 with 9 (k_3) would be slower than reaction of 9 with cyclohexadienyl radical (k_d) by about the same amount. If this were rigorously true, we would have C = 1. We have taken C = 0 in Calculation 1, but explore nonzero values in subsequent calculations.

(4). The parameter $D \equiv k_r / k_3^{\frac{1}{2}}$ controls the decyclization of ring-cyclized 9 to ring-opened 3. We have previously argued that decyclization must be a minor factor under conditions employed in this work (pp. 114, 115). Therefore, we have taken D = 0 for the present, but will later determine how large a value can be accommodated by the data.

As the effect of decyclization on the product ratio R1 should be most pronounced at the lowest initial perester concentrations investigated (p. 114) we have assigned RWT1 = 0 for a number of such runs (see Table 17). This will insure that we do not prejudice the calculated values of R1 at lower perester concentrations, should decyclization be detectable with the present data, by obliging the computer program to distribute any inability to fit the R1 ratios over runs where the mechanistic assumption of no reversibility of the ring cyclization is really inadequate. In this way, systematic errors in the $R1^{calc}$ at low perester concentrations will give a reliable measure of how large D might be.

(5). The parameters γ, δ, and ϵ: The parameter γ describes the probability of getting 10 plus tetrahydronaphthalene, rather than dimer, from the reaction of a pair of ring-cyclized radicals. Similarly, δ and ϵ describe what happens upon reaction of a ring-cyclized radical with a cyclohexadienyl radical (see Chart 7, p. 198). We have previously argued that the average efficiency of conversion of 9 to dihydronaphthalene 10 must be about 40% for reaction in 1,4-cyclohexadiene (pp. 122, 123). As our calculations indicate that reaction of 9 with a cyclohexadienyl radical is a good deal more probable than reaction of a pair of ring-cyclized radicals, this means that we must have $\delta \sim 0.4$. Actually, but equivalently, the values $\frac{1}{2}\gamma = 0.30$ and $\delta = 0.42$ we have routinely employed were chosen to give the predicted yields of ring-opened hydrocarbon 5 approximately correctly. With these values, the predicted yields of 5 may be too high or too low, on the average, but not by more than 3% in any calculation reported. This insures that values of $E = k_a^{⌬}/k_r$ found in the calculations (about 0.14 at 100°) are realistic.

We have assumed that δ and γ are not temperature dependent. As, for example, the ratio of disproportionation to combination decreases from 0.34 to -191° to 0.15 at 85° for ethyl radicals in isooctane (103), some comment on the validity of this assumption is in order. To begin with, even should δ and γ vary smoothly by a factor of two between 0 and 150°, the ability of the mechanistic scheme to correlate the product ratios would not be seriously impaired. The reason is that the calculated values of R1 essentially depend on the ratio E/δ, so that an error in the assumed temperature dependence of δ would simply produce a corresponding error in the temperature dependence found for E. At the same time, R2 depends essentially on G/E, so that the temperature dependence of G would also be distorted. On the other hand, calculated yields of the hydrocarbon $\underset{\frown}{5}$ depend strongly on E but only weakly on δ. Thus, if the latter were appreciably temperature dependent, the calculated yields of $\underset{\frown}{5}$ should be systematically high at one end of the temperature scale and low at the other. Analysis of the calculated yields of $\underset{\frown}{5}$ (Table 17, p. 297) reveals that any such systematic error must be small.

(6). The composite activation energies of the parameters F and H have been fixed at 0 and -8 kcal/mole, respectively, for most calculations. The reasoning behind these choices will be considered later.

The parameters subjected to iterative improvement are E, F, G, H, and I. As noted previously, each of these is described by a modified Arrhenius equation (eq. 2.2-23, p. 224) in terms of the value at 100° (optimized for all five) and a composite activation energy (optimized for E, G, and I). Values found for these quantities are recorded in Table 19, p. 303).

C. Tabulation of Quality-of-Fit Quantities and Other Information

A final point before considering in detail the results of the calculations concerns the way in which pertinent information has been recorded. Basically the problem is that the amount of space, time, and money which would be required to record all of the information generated by the computer program for each of the calculations here reported on would be prohibitive. Still, sufficient information must be given to enable the reader to judge the success of various calculations or to explore further points of special interest. The fortunate fact that features which distinguish the various calculations are generally fairly minor ones suggests a compromise procedure in which results are presented at three levels of sophistication:

(1). All calculations are represented in Table 19 (p. 303), where (a) several quantities related to the quality of the fit to the experimental data and (b) the parameter values assumed or found via least-squares optimization are recorded.

(2). For approximately half of the calculations we shall additionally record, for each of the runs, the calculated ratios R1 and/or R2 and the percent relative deviations (RELDEV) between predicted and observed product ratios. This information appears in Table 18 (p. 299).

(3). Finally, Table 17 (p. 296) gives a complete set of information for the calculation which appears to be the most satisfactory regarding the quality of the fit and the soundness of the mechanistic assumptions. This includes experimental information recapitulated for convenience from Tables 1, 2, 4, 5, and 6 in addition to calculated values for a number of quantities of interest besides the ratios R1 and R2.

Tables 17 and 18 have been made vertically compatible so that entries for the same runs (each of which is assigned a run number) can be compared fairly easily. The solid horizontal lines in Tables 17 and 18 serve to compartmentalize the tables into regions corresponding to the earlier data tables; working from the top down, the order of presentation is Table 2, Table 1, Table 6, Table 4, Table 5. Dashed lines between the solid lines in the regions of Tables 2 and 1 separate runs at different temperatures.

We shall now introduce the quality-of-fit quantities tabulated in Table 19. The quantity RUSD, the relative unbiased standard deviation, is defined in eq. 2.4-1,

RUSD =

$$\left[\frac{\sum_{i=1}^{N}\left\{\left[\frac{R1_i^{calc}-R1_i^{obs}}{R1_i^{obs}}\right]^2 RWT1_i+\left[\frac{R2_i^{calc}-R2_i^{obs}}{R2_i^{obs}}\right]^2 RWT2_i\right\}}{\frac{1}{2N}\sum_{i=1}^{N}\{RWT1_i+RWT2_i\}\ (2N-10)}\right]^{\frac{1}{2}} \qquad (2.4\text{-}1)$$

where:

$$RWT1_i \equiv (R1_i^{obs})^2/L1_i \qquad (2.4\text{-}2)$$

and similarly for $RWT2_i$.

The sum in the numerator of eq. 2.4-1 is simply S (eq. 2.3-1), the sum of the squares of residuals we wish to minimize. This recognition throws light on the meaning of the relative weight quantities

RWT1 and RWT2. Values of these quantities for Calculation 14 are recorded in Table 17. Those for all other calculations were very similar.

The quantity (1/2N) times the sum of the relative weights is simply the average relative weight. The quantity (2N - 10) plays the role of the 'number of observations less one' in the perhaps more familiar relationship for the relative unbiased standard deviation of the mean of a series of measurements on a single quantity. Here, however, we are instructed to divide by the number of degrees of freedom--the number of observations less the number of adjustable parameters (26). The correct value for the latter is uncertain, but 10 will not be too far off. The problem is that there are more than 10 'parameters' which have to be specified for each iteration, but a number of these are obtained other than with reference to the quality of the fit to the product ratio data.

Finally, the expression for RUSD is actually slightly more clever than indicated in eq. 2.4-1 in that provision has been made for omitting certain of the data points for each product ratio from the least-squares fit. Such cases can be recognized in Table 17 by $RWT1_i$ or $RWT2_i = 0$ and are designated for calculations appearing in Table 18 by enclosure of the RELDEV quantities (see below) in parentheses. The result is that certain terms will make no contribution to the sums in eq. 2.4-1 and 2N must be replaced by the actual number of product-ratio observations included in the iterative procedure.

As minimization of RUSD with respect to the parameters differs from the minimization of S only to the (very minor) degree that specific values of the parameters effect the average RWT, RUSD is an appropriate quantity for comparing the success of various calculations. However, the relationship between RUSD and the quality of the fit seems to us less perspicuous than a measure of the average relative deviation between calculated and observed product ratios. Therefore, we shall generally quote[*]

$$\text{AVDEV} = \frac{\sum_{i=1}^{N} \left\{ \left| \text{RELDEV R1}_i \right| \text{RWT1}_i + \left| \text{RELDEV R2}_i \right| \text{RWT2}_i \right\}}{\sum_{i=1}^{N} \{\text{RWT1}_i + \text{RWT2}_i\}} , \qquad (2.4\text{-}3)$$

where:

$$\text{RELDEV R1}_i \equiv \left\{ \frac{\text{R1}_i^{\text{calc}} - \text{R1}_i^{\text{obs}}}{\text{R1}_i^{\text{obs}}} \right\} \times 100\% \qquad (2.4\text{-}4)$$

and similarly for RELDEV R2_i.

In comparing various calculations, we shall often be interested in the effect of alternative assumptions on how well the ratios R1 and R2 are individually described; or, for the ratios R2, say, whether the

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[*] There is some question as to whether RWT1 and RWT2 or their square roots should be used as weighting factors in eq. 2.4-3. On first glance, comparison of eqs. 2.4-1 and 2.4-3 supports the latter alternative. However, we believe that the correlation between AVDEV and RUSD will be superior with eq. 2.4-3 defined as is.

average relative deviation reflects principally a lack of success in fitting the data from one or the other of the peresters. That is, a breakdown of AVDEV into various components is potentially of interest. Therefore, we have also recorded in Table 19 the quantities AVDEV R1, AVDEV R2, AVDEV $R1_1$, AVDEV $R1_2$, AVDEV $R2_1$, and AVDEV $R2_2$, where the subscripts to the last four quantities designate the starting perester.

D. Systematic Errors in Calculated or Observed Product Ratios and Suggested Mechanistic Modifications

In assessing the quality of the fit of an assumed relationship to experimental data, two types of considerations are in order. The first is whether the average deviation between calculated and observed quantities is compatible with experimental error. The second is whether such deviations are random, or whether they tend to correlate with environmental factors such as time of observation or details of the experimental procedure.

In the present case, any such correlation should be most apparent in terms of the behavior of the RELDEV quantities (eq. 2.4-4) as a function of reaction temperature or reagent concentrations. Lack of any pattern in the signs and magnitudes of these quantities would suggest that errors of mechanistic oversimplification are less important than experimental errors. Conversely, the presence of sizable systematic errors would point either to inadequate mechanistic assumptions or to systematic errors in the experimental observations.

Calculations based on the simplest interpretation of the mechanistic scheme of Chart 7 do show systematic errors which transcend in magnitude and regularity mere statistical fluctuation. We shall show that allowance for medium effects on the rate 'constants' for certain processes can explain subtleties in the product-ratio data of two kinds which appear to be otherwise inexplicable. One such modification consists in a reciprocal dependence of rate constants for diffusion-controlled processes on the viscosity of the medium, as suggested by theoretical treatments based on hydrodynamic models of the liquid state (e.g., eq. 2.4-7). The other involves the postulation of solvation effects on competitive processes; such effects seem not to have been previously implicated for reactions of nonpolar hydrocarbon radicals.

Deployment of these modifications reduces AVDEV from 6.1% in Calculation 1 to 4.4% in Calculation 15. The figures themselves are not greatly different, but we are inclined to the view that the latter figure represents essentially the accuracy of the data and hence that the improvement is significant.

Consideration of alternatives may appear excessive, but we have wished to put the case as strongly as possible, as a general recognition of such medium effects, and particularly of solvation effects on nonpolar hydrocarbon radicals, would represent a considerable departure from what we feel to be the present view of radical reactions. The present data do not allow the conclusion that medium effects of the two types have been demonstrated experimentally. But this is principally because our experiments have not been designed for that purpose; we have had other concerns. Perhaps the expositions under headings (2) and (3) below will prove sufficiently provocative or suggestive to engender adequate experimental tests.

(1). R1 with Reaction Temperature

The systematic error here is easily detected upon comparison of the fit to the R1 ratios for perester 2 at 70° (runs 9–12) with that for perester 1 at 99° (runs 13–17). We find for Calculation 1 (Table 18) that RELDEV R1[*] averages + 14% for runs 9–12 and - 12% for runs 13–17; the R1 ratios for the two peresters do not mesh smoothly as a function of reaction temperature.

This incompatibility can be at least partially redressed by allowing disproportionation of ring-cyclized 9 with ring-closed 4 to give 10 plus 6. As yields of 6 are derived principally via disproportionation of 4 with cyclohexadienyl radical, and as these yields are more than an order of magnitude larger when 2 is employed as starting perester rather than 1, we must expect that the reaction 4 + 9 will increase yields of 10 to a greater degree at 70° for perester 2 than at 99° for perester 1. As R1 is defined to be % yield 5/% yield 10, the former ratios, which are presently too high, will thus be selectively reduced. Thus, in Calculation 2 (Table 18) we have taken C = 1, which is the expected value according to point (3), page 242. We now find that

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[*] RELDEV quantities are defined to be (calculated–observed)/observed. Thus, positive RELDEV implies that the calculated result is too high.

RELDEV R1 averages + 13% at 70° and - 11% at 99°. In practice, therefore, reaction of 4 plus 9 is not of much help.

No other mechanistic modifications capable even in principle of repairing the temperature discontinuity come to mind. Neither is it clear why either the 70° or the 99° R1 data should be subject to unusually large experimental error. For the present, the origin of the temperature discontinuity must remain unexplained.

(2). R2 with 1,4-Cyclohexadiene Concentration

Looking again at Calculations 1 and 2, we note that AVDEV for C = 1 (6.82%) is substantially greater than for C = 0 (6.07%). A major reason for the less satisfactory fit is that C = 1 exacerbates already significant systematic deviations which show up in the product ratios R2 from perester 2. We have in runs 1–12 three sets of four experiments featuring a range of 1,4-cyclohexadiene concentrations. Within each of the sets, there is a remarkable tendency to have RELDEV large and positive for the ~ 3 M run and large and negative for the ~ 10 M run, with appropriate gradations in between. The worst case is the set of four runs at 0°, where RELDEV (run 1)–RELDEV (run 4) = 19% in Calculation 1 and 24% in Calculation 2.

This is a sizable systematic error, and one which we must deal with, if we can. Four suggestions may be advanced.

(a). The error might arise from inadequacy of the assumption that formation of products from radicals 3 and 4 is much slower than their interconversion. It can easily be shown that partial trapping of 4 (starting from ring-closed perester 2) can be described with high accuracy by replacing the expression for $R2^{calc}$ by $R2^{calc} \times (1 + k_a^{⌬}(ZH)/k_1)$. As the correction term will selectively increase R2 at the higher 1,4-cyclohexadiene concentrations, partial trapping could in principle explain the pattern of the observed deviations. However, using eqs. 1.7-6 (p. 102) and 1.8-12 (p. 138) we can write

$$k_a^{⌬}/k_1 = 2.3 \times 10^{-2} \exp(1.5/RT) \quad . \qquad (2.4\text{-}5)$$

At 70° this rate-constant ratio has a value of 0.002, so that for ~ 10 M 1,4-cyclohexadiene the multiplicative correction term is 1.02. Thus, the assumption of rapid equilibration of 3 and 4 is valid in the present circumstances.

(b). Our mechanistic scheme assumes that interactions of ring-cyclized radicals in pairs or with cyclohexadienyl radicals may result either in disproportionation or in coupling. In contrast, we have assumed that the reaction of ring-closed radical 4 with cyclohexadienyl radical always yields 6 (plus benzene). Other outcomes are at least possible.

The effect on the R2 ratios of allowing for the alternative disproportionation (to give the methylenecyclopropane 16) or for coupling is to reduce the systematic error under discussion. That this should be the case can be inferred from the mechanistic equations, but the reasoning is complex and need not concern us here; trial calculations show that incursion of the alternative reactions to the maximum extent allowed by the data is ineffective in redressing the systematic bias. To make headway, we must assume that only one reaction in three of 4 with cyclohexadienyl radical yields 6. As yields of the methylenecyclopropane are substantially independent of the initial perester concentration (see Table 6), this partitioning ratio would imply that the coupling product is formed in approximately twice the yield of 6, or approximately 30% for runs 1–12. This is physically impossible: the deficit in material balances for vpc-detected momomeric products is only about 10% for these runs (p. 123). Moreover, the major portion of this deficit is attributable to dimer formed from ring-cyclized radicals (p. 282).

(c) $R2^{calc}$ goes approximately as the square root of the rate of decomposition of perester (see below, p. 257 , eq. 2.4-11). Thus, a solvent effect which had k_o approximately 60% greater in 1,4-cyclohexadiene than in cyclohexane could repair the systematic nature of the deviations. A solvent effect of this magnitude would probably not be expected, but can not be ruled out in the absence of actual rate measurements. However, such an explanation would be *ad hoc*, and we can rationalize the systematic bias in a perfectly natural way, as in (d).

(d) The rate constant k_D of a diffusion-controlled reaction is often expressed in terms of the so-called Smoluchowski equation,

$$k_D = 4\pi r_{AB} D_{AB} \quad , \tag{2.4-6}$$

where r_{AB} is the sum of the radii of reactants A and B (the collision radius), and $D_{AB} = D_A + D_B$ is the diffusion coefficient for relative motion of A and B. By replacing the diffusion coefficient in eq. 2.4-6 using the Stokes-Einstein relationship for molecular particles (104).

$$D = kT/4\pi\eta r_s \quad ,$$

Debye obtained eq. 2.4-7, where r_s is the hydrodynamic radius of a diffusing particle (which we have taken to be the same for A and B)

$$k_D = 2r_{AB}RT/10^3\eta r_s \tag{2.4-7}$$

and η is the viscosity of the medium (105).

Except at very low initial concentrations of perester **1**, where a sizable part of the diphenylcyclopropylmethane **6** is formed via abstraction of hydrogen from 1,4-cyclohexadiene, $R2^{calc}$ is roughly proportional to $k_b^{\odot}$, the rate constant for transfer of a hydrogen atom from cyclohexadienyl radical to **4**. From eq. 2.4-7, we should therefore expect $R2^{calc}$ to be inversely proportional to the viscosity of the medium if the $k_b^{\odot}$ process is diffusion-controlled, as it may well be.

On the basis of these considerations, the viscosity of 1,4-cyclohexadiene--cyclohexane mixtures was investigated at 20°. As shown in Fig. 21, the viscosity of cyclohexane (0.96(106)) is ~1.6 times that of 1,4-cyclohexadiene (determined to be 0.60). As is usual with binary mixtures, the viscosity of the mixture is quadratic, rather than linear, in the mole (or volume) fractions of the components (107).

The line drawn is for

$$\eta_{\text{mix}} = \eta_{\text{⌬}} + \left(\eta_{\text{⬡}} - \eta_{\text{⌬}}\right)x^2 \quad . \qquad (2.4\text{-}8)$$

where x is the volume fraction of cyclohexane. If we define $\phi \equiv \eta_{\text{⬡}}/\eta_{\text{⌬}}$, we can write

$$\eta_{\text{⬡}}/\eta_{\text{mix}} = \phi / 1 + (\phi - 1)\,x^2 \quad , \qquad (2.4\text{-}9)$$

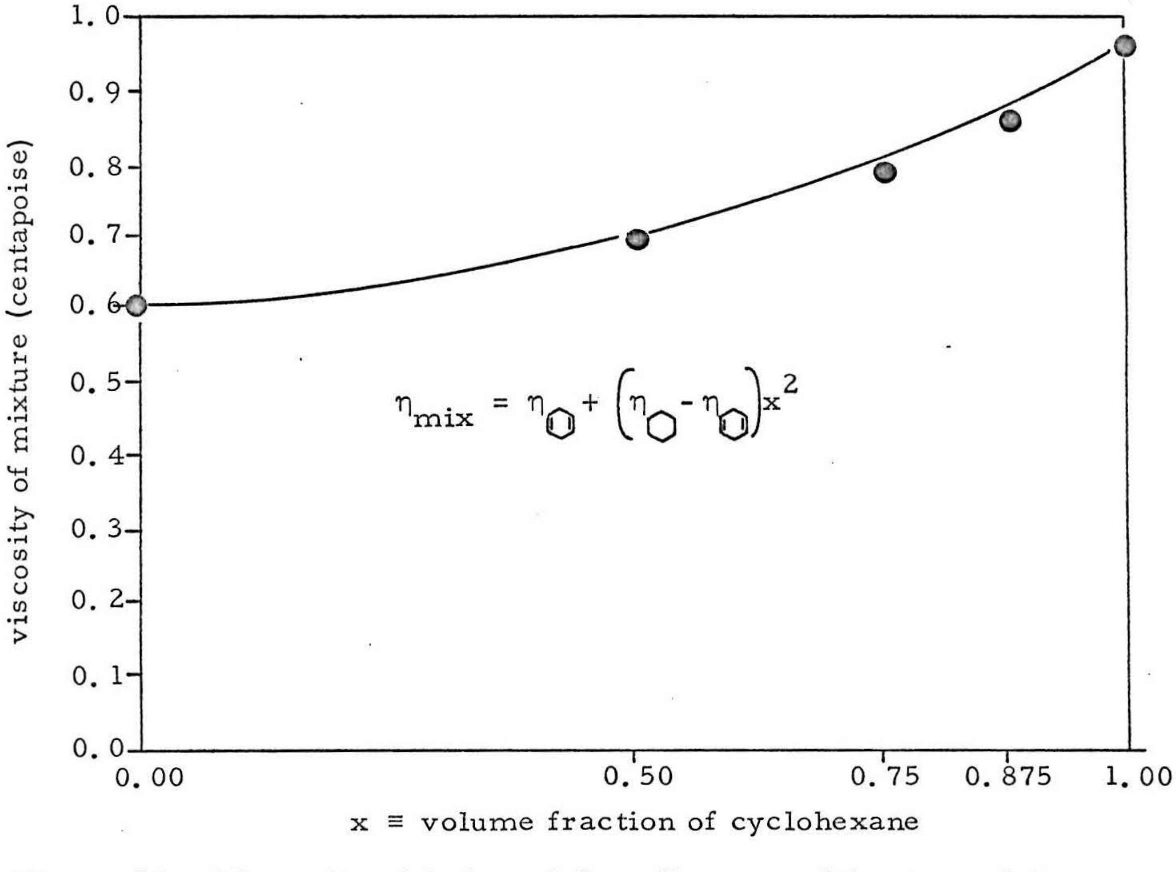


Figure 21. Viscosity of 1, 4-cyclohexadiene—cyclohexane mixtures at 20°.

so that using eq. 2. 4-7 we have

$$\left(k_b^{\text{⏣}}\right)_{mix} = \left\{\phi/\left(1 + (\phi-1)x^2\right)\right\}\left(k_b^{\text{⏣}}\right)_{\text{⬡}} . \qquad (2.4\text{-}10)$$

Thus, $k_b^{\text{⏣}}$ is predicted to increase with increasing 1,4-cyclohexadiene concentration, so that $R2^{calc}$ can be made to decrease less rapidly with increasing cyclohexadiene concentration than predicted in Calculations 1 and 2. This is the type of correction required to smooth out the systematic deviations found for those calculations.

If we write

$$\frac{d(\underset{\sim}{6})}{d(\underset{\sim}{5})} \cong \frac{k_b^{\text{⏣}}(Z\cdot)(\underset{\sim}{4})}{k_a^{\text{⬡}}(ZH)(\underset{\sim}{3})} = \frac{k_1 k_b^{\text{⏣}}}{k_2 k_a^{\text{⬡}} k_4^{\frac{1}{2}}(ZH)} (\alpha k_o(P)/2XF)^{\frac{1}{2}} , \qquad (2.4\text{-}11)$$

using the definitions of X and F given previously (pp. 203, 206) we see that formally we must also account for the effect of viscosity on the square root of the rate constant, k_4, for bimolecular reaction of cyclohexadienyl radicals. The effect, within this simple scheme, is to make $R2^{calc}$ dependent on $\left\{\phi/(1 + (\phi-1)x^2)\right\}^{\frac{1}{2}}$. The exact relationship is obtained by replacing G in eqs. 2.1-1—2.1-10 by

$$G = G(x,\phi) = G_{\text{⬡}} \ \phi/ \ 1 + (\phi-1)x^2 \ ^{\frac{1}{2}} , \qquad (2.4\text{-}12)$$

where $G_{\text{⬡}}$ (tabulated in Table 19 as G for calculations where $\phi \neq 1$) is the value of G in cyclohexane solution.

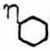
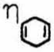
The viscosity data can be described more accurately than by the line shown in Fig. 21 by including a linear term in x in eq. 2.4-8. However, the simple relationship of eq. 2.4-8 has been employed to make explicit our expectation that the shape of the viscosity—

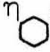
composition relationship will be simply related to the viscosity difference for the pure components. Some such assumption about the shape of the relationship is needed because ϕ may well be temperature dependent. Viscosity data for benzene ($\eta(20^\circ) = 0.65$) between 0 and 80°(108) and for cyclohexane between 15 and 250°(106) were fitted to the Arrhenius equation. The two relationships were then combined to give

η$/\eta$ $= (0.41 \pm 0.02) \exp(0.73 \pm 0.04)/RT)$. (2.4-13)

Benzene, the less viscous at 20°, is predicted to be the more viscous at high temperatures (above 140°).

By rough analogy with this result, we have taken

η$/\eta$ $\equiv \phi = 1.00 \exp(0.274/RT)$ (2.4-14)

in Calculation 3. This relationship gives $\phi(20^\circ) = 1.6$ but assumes that the ratio η$/\eta$ will decrease with increasing temperature, so that the viscosity correction to $R2^{calc}$ will become less important.

Results for the R2 ratios for Calculation 3 are shown in Table 18, with quality-of-fit quantities in Table 19. From the latter, we see that while AVDEV (5.94%) is only about 0.1% better than in Calculation 1, AVDEV $R2_2$ has been reduced by 0.6%. Moreover, on examining RELDEV quantities in Table 18, we find that RELDEV R2 (run 1) - RELDEV R2 (run 4) is 5.6% as compared to 19% in Calculation 1: the systematic error with 1,4-cyclohexadiene concentration has virtually been eliminated from the R2 ratios.

Calculation 4 is the same as Calculation 3, except that we have taken $\phi = 1.6$, independent of temperature. Quality-of-fit quantities in Table 19 show that this assumption gives only a slightly less satisfactory fit to the ratio data.

For all remaining calculations, we have described ϕ via an equation of the form of eq. 2.4-14; i.e., with a preexponential factor of unity and a composite activation energy which gives $\phi(20^\circ)$ as recorded in Table 19.

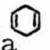
In Calculation 2 we took C = 1 and found the fit to be substantially worse than in Calculation 1 for C = 0. With $\phi(20^\circ) = 1.6$, however, setting C = 1 in Calculation 5 (Tables 18, 19) improves the quality of the fit. Calculations 6–10 (Table 19) demonstrate that the pairing of C = 1, $\phi(20^\circ) = 1.6$ is about the optimum combination.

(3). R1 with 1,4-Cyclohexadiene Concentration

As can be seen for Calculation 14 (Table 17), the $R1^{calc}$ tend to deviate negatively at low cyclohexadiene concentrations and positively at 8–10 M cyclohexadiene; swings of 20–30% in the RELDEV R1 quantities are common. Note that the observed reduced ratios in column 2, p. 297 vary much more sizeably than do the calculated values recorded in column 3. These quantities were defined (eq. 1.8-5, p. 111) to be proportional to $k_r/k_a^{⌬}$, where the proportionality constant is the fraction of ring-cyclized radicals which are converted to the dihydronaphthalene **10**. Superficially, at least, this makes it appear that the mechanistic scheme predicts the efficiency of conversion of **9** to **10** to be less variable than actually is the case. The current parameterization $\gamma = 0.60$, $\delta = 0.42$ implies conversion efficiencies of 30% for pairwise reaction of ring-cyclized radicals and of 42% for reaction of ring-cyclized radicals with cyclohexadienyl radicals; clearly, little variability in the overall conversion efficiency is possible under this parameterization.

We can maximize the variability by making the outcome for reaction of 9 with 9 as different as possible from that for reaction of 9 with cyclohexadienyl radical. If we choose $\gamma = 0$, we find that $\delta = 0.45$ is required to get the average yield of ring-opened hydrocarbon 5 right. The effect of this parameterization on the R1 ratios can be seen in Table 18 for Calculation 11. We now have AVDEV = 5.03% compared to 5.76% for Calculation 5. However, we find that while the systematic error in RELDEV R1 with cyclohexadiene concentration has been essentially removed from the perester 1 runs (runs 13-26), the situation is not greatly improved for the perester 2 runs (runs 1-12). We conclude that variation of conversion efficiency alone is not capable of fully redressing the systematic nature of the deviations.

A serious objection to the parameterization $\gamma = 0.00$, $\delta = 0.45$ is that a much higher value for γ seemed to be required to account for experimental observations for reaction in triethyltin hydride. To recount the situation, the mechanistic treatment of induced decomposition gave results compatible with rate accelerations and with observed yields of the cage ether 12, provided that ring-cyclized radicals were allowed to react with triethyltin radicals only infrequently (pp. 170-179). At the same time, consideration of material balances required that 9 be converted to 10 with an efficiency of at least 30% (pp. 133, 134). The implication is, then, that $\gamma \geq 0.6$. For this reason, we reject the parameterization of Calculation 11, even though mathematically it represents a substantial improvement.

Returning again to a consideration of the reduced ratios of Table 17, the other possibility* is that the efficiency of conversion of 9 to 10 is sensibly constant, but that k_r/k_a itself increases with increasing cyclohexadiene concentration. As these processes are not diffusion-controlled, the viscosity effect considered under the previous heading would presumably not be a factor. However, association of radical intermediates with the π-bonds of the olefinic 1,4-cyclohexadiene might measurably affect the rate constants for the two processes. Presumably, the saturated co-solvent cyclohexane would simply act as a space filler.

Medium effects involving solvation of radical intermediates have been generally recognized for approximately the last decade. A review article covering the literature through 1964 has been supplied by Huyser (66). Extensive work has been done on the effects of complexing of chlorine radicals and alkoxy radicals with various solvents, notably olefinic and aromatic materials. In contrast, Huyser is able to report only one well-supported example of a medium effect of the type we are considering here on hydrocarbon radicals, and that example concerns the trichloromethyl radical. This suggests that

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[*] Failure to account for significant hydrogen abstraction by 3 from cyclohexane could in principle explain the observed behavior. However, 21 the saturated analog of 3, abstracts hydrogen from 1,4-cyclohexadiene about 250 times as rapidly as from cyclohexane (see the footnote to p. 335). As the smallest mole ratio of 1,4-cyclohexadiene to cyclohexane is ~1:10, neglect of hydrogen abstraction from the latter is apparently not serious.

'large' solvent effects will be absent unless the possibility exists for polar interactions between the radical intermediate and the solvent.

However, we shall require, to repair the systematic error under discussion, that k_r/k_a vary by only ~30% between pure cyclohexane and pure cyclohexadiene; and as solvents may effect the reactivity or relative reactivity of chlorine or alkoxy radicals by up to two orders of magnitude, for presently known cases, it would seem improper to reject out of hand the possibility of solvent effects on nonpolar hydrocarbon radicals of the much smaller magnitude we have in mind.

As is well known, *t*-butoxy radicals may abstract hydrogen from solvent or may undergo β-scission to give acetone plus a methyl radical. This competition, which has been extensively investigated by Walling and Wagner, can perhaps serve as a model for the competition between hydrogen abstraction and ring-cyclization by ring-opened radical **3**. One of Walling and Wagner's experimental observations is that complexing solvents favor decomposition (the scission process) over hydrogen abstraction (42). Not only olefins and aromatic hydrocarbons but also polar materials such as acetic acid and acetonitrile have this effect. This was taken to suggest that part of the effect is due to solvation of a decomposition transition state which involves charge separation as a consequence of the polar nature of the product acetone. However, solvent effects were also observed on the relative rates of abstraction of primary and tertiary hydrogens from 2,3-dimethylbutane, suggesting that the medium must also influence the rates of hydrogen-abstraction reactions. The main element of the interpretation here is that solvation must be at least partially broken to allow the prospective hydrogen donor to properly approach the radical center. If applicable to our situation, this would suggest that complexing of the radical center in 3 with the π-bonds of 1,4-cyclohexadiene should disadvantage hydrogen abstraction from 1,4-cyclohexadiene with respect to the intramolecular <u>ortho</u>-ring cyclization. As a result, $k_r/k_a^{\text{⬡}}$ should increase with increasing 1,4-cyclohexadiene concentration, as required to repair the systematic errors in R1.

To see how great an improvement might result from invoking such a solvent effect, Calculation 12 was carried out where we have replaced $E = k_a^{\text{⬡}}/k_r$ (independent of solvent composition) by

$$E = E_{\text{⬡}}\{1 - 0.0076 * \exp(0.72/RT) * (ZH)\} \qquad (2.4\text{-}15)$$

where $E_{\text{⬡}}$ is the value of E in cyclohexane. This relationship causes E to vary linearly with cyclohexadiene concentration by 30% at 0° and 15% at 150° between pure cyclohexane and pure cyclohexadiene. Of course, a linear relationship is not required by any available information, but seems not unreasonable. The lesser effect at 150° is compatible with the demands of the data and with the expectation that association between various species will be broken by higher temperatures.

The quality-of-fit quantities in Table 19 show that a beginning has been made. Specifically, AVDEV R1, at 5.12%, is ~3.5% lower than in Calculation 5 and even 1.4% lower than in Calculation 11. The greatest improvement is shown by the AVDEV $R1_2$ quantities: 10.65%

for Calculation 5; 8.38% for Calculation 11; but only 5.74% for Calculation 12. The reason for this improvement is easily seen in the RELDEV R1 quantities for Calculations 5, 11, and 12 in Table 19; the systematic drift with cyclohexadiene concentration of Calculation 5, only partially repaired in Calculation 11, is hardly detectable in Calculation 12.

However, the AVDEV R2 quantities are so adversely effected that AVDEV itself is higher in Calculation 12 than in either 5 or 11. The reason is not hard to determine; the RELDEV R2 quantities for Calculation 12 (especially for runs 1–12) again vary systematically with the 1,4-cyclohexadiene concentration, but now in the sense <u>opposite</u> to that we sought to correct under the previous subheading.

The reader can verify from eqs. 2.1-4 and 2.4-11 that

$$R2^{calc} \cong \left[\frac{k_1}{k_a^{\text{⬡}}}\right]\left[\frac{k_b^{\text{⌬}}}{k_2}\right]\frac{(Z\cdot)}{(ZH)} \sim G/E \quad . \qquad (2.4\text{-}16)$$

Eq. 2.4-16 shows that the variation of E given by eq. 2.4-15 is carried directly over onto the R2 ratios although this is not logically required. In line with the reasoning given above, we might expect that solvation of $\underset{\frown}{3}$ and $\underset{\frown}{4}$ by cyclohexadiene will favor $k_a^{\text{⬡}}$ over k_1 and $k_b^{\text{⌬}}$ over k_2, but perhaps less strongly in the latter case; a relatively stable dibenzylic radical such as $\underset{\frown}{4}$ may be less susceptible to interactions with the environment of any type than a primary radical such as $\underset{\frown}{3}$. Thus, G/E should vary with the cyclohexadiene concentration, but probably not as strongly as does 1/E.

To see what degree of compensation by G would be required to put the R2 ratio situation right,[*] a series of calculations was begun using

$$G = G(x,\phi)\ \{1 - 0.0038*\exp(0.72/RT)*(ZH)\}\quad , \qquad (2.4\text{-}17)$$

where $G(x,\phi)$ is given by eq. 2.4-12. (Comparison to eq. 2.4-16 shows that this corresponds to allowing G to compensate for half the variation built into E.) However, the results were so favorable that only this first calculation, Calculation 13, was carried out. We now find that neither the R1 nor the R2 ratios show significant systematic deviations as a function of 1,4-cyclohexadiene concentration (see Table 18, p. 301). Furthermore, AVDEV (Table 19) has decreased to 4.57%, a figure which is much superior to any previously discussed.

The major remaining problems are the temperature incompatability between 70 and 99° for the R1 ratios (although, with variation of E, this is less severe than previously) and the major discrepancy between calculated and observed R2 ratios for runs 31–35. The latter is discussed under (4) below.

(4), R2 Values from Table 4

A systematic deviation which shows up in all the calculations concerns the R2 ratios from the Table 4 concentration study (runs 31–35). Both the calculated and observed ratios decrease with

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[*] There are, of course, alternatives. To cite two, we could increase C (compare Calculations 1 and 2) or we could decrease $\phi(20^\circ)$.

decreasing initial perester concentration, but the calculated ratios are consistently, and seriously, too low. In view of the general success of the mechanistic scheme in smoothly correlating widely varying R2 ratios for both peresters, we may perhaps suggest that yields of ring-closed hydrocarbon 6 (which range from 0.3% to 0.1%) are simply in error for runs 31–35. We noted previously (pp. 116 - 118) that commercial 1,4-cyclohexadiene generates upon heating one or more impurities which could be mistaken for 6; perhaps this complication was especially troublesome in these runs.

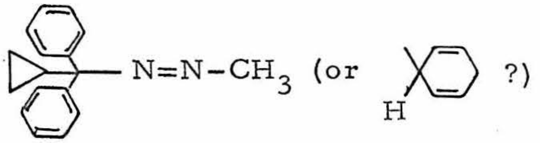
In any case, the R2 ratios for runs 31–35 were assigned zero weight in all the calculations. This has two effects: (a) quality-of-fit quantities are improved; and (b) the possibility is avoided of seriously distorting values of various parameters in a vain attempt to accommodate erroneous experimental data.

E. Prospects for Experimental Verification of Medium Effects on R1 and R2

Although precedent exists only for the viscosity correction to $R2^{calc}$, both this and the solvation correction to E and G are capable of explaining experimentally significant systematic deficiencies in the calculated product ratios. It seems feasible to determine whether these mathematical innovations reflect physical reality.

A test of the importance of solvent effects on the R1 ratios could be made by measuring R1 at $\sim 0^{\circ}$ for a series of reactions approximately 1 M in 1,4-cyclohexadiene in which the cosolvent is varied from pure cyclohexane to pure cyclohexene. The latter would presumably complex ring-opened radicals about as well as the unconjugated 1, 4-cyclohexadiene, but would not be comparably active as a hydrogen donor. The information necessary to correct for hydrogen abstraction from cyclohexene in the terinary mixtures could be obtained by running 2 in neat cyclohexene. One would of course want to use fairly low initial concentrations of 2 (perhaps 0.01 M) in order to minimize any uncertainty in the 1, 4-cyclohexadiene concentrations arising from uncertainty in the amount consumed in the reaction.

The viscosity dependence seems to be on reasonably solid theoretical ground. One might therefore look ahead to experiments which would simultaneously establish unambiguously the reality of the effect and put it to good use. If, for example, the azo compound shown below could be made, decomposition in approximately 1 M 1, 4-cyclohexadiene in a range of co-solvents would allow one to simultaneously monitor the



influence of the principal solvent (a) at keeping 4 and cyclohexadienyl radical apart and (b) at keeping 4 and methyl radical together (as measured by the effect of solvent on the efficiency of cage recombination). Ring-closed perester 2 would be less satisfactory than the azo compound because of the apparently limited stability of the combination product, the ring-closed *t*-butyl ether 15 (pp. 78, 79). The point would be to quantify and explore the limitations of the anticipated reciprocal influence of viscosity on cage recombination and on rate constants for diffusion-controlled processes.

F. Hydrogen Abstraction by Lactonyl Radicals from 1,4-Cyclohexadiene

Calculations 1–13 have employed the parameterization

$$B \equiv k_5k_d/k_6k_3^{\frac{1}{2}} = 1.00 \exp(-12/RT) \qquad (2.4\text{-}18)$$

where k_5 and k_6 are the rate constants for hydrogen abstraction by lactonyl radicals (22) from 1,4-cyclohexadiene and cyclohexadienyl radical, respectively, and k_d and k_3 are the rate constants for the radical-radical reactions 9 + cyclohexadienyl and 9 + 9, respectively. During the period in which nearly all of the calculations were carried out, we erroneously had $B \equiv k_5/k_6$. The parameterization of eq. 2.4-18 seemed reasonable under this incorrect definition, but now appears indefensible (see below). Its effect is to have hydrogen abstraction by 22 occur almost totally from cyclohexadienyl radical. We found, in a series of calculations leading up to Calculation 1, that just this circumstance was required to obtain the best fit to the ratio data.

We seek here to determine the effect on the calculations of 'reasonable' parameterization for B. Fortunately, we have in the hydrogen-abstraction reactions of the dibenzylic ring-closed radical 4 an excellent model for the k_5 and k_6 reactions of the dibenzylic lactonyl radical 22. The reader can confirm from the parameter definitions of eqs. 2.1-4 that

$$k_b^{\bigcirc}k_d/k_b^{\odot}k_3^{\frac{1}{2}} = E{*}I/G \quad . \qquad (2.4\text{-}19)$$

From typical values of E, I, and G listed in Table 19, we can write

$$k_b^{\text{⬡}} k_d / k_b^{\text{⌬}} k_3^{\frac{1}{2}} \cong 6 \times 10^2 \exp(-10.5/RT) \quad . \qquad (2.4\text{-}20)$$

If the rate-constant ratios for hydrogen abstraction from 1,4-cyclohexadiene and from cyclohexadienyl radical are identical for 4 and for 22, B can be equated to the right-hand side of eq. 2.4-20.

Calculations 5, 11, and 13 were therefore repeated using this parameterization, but with all other non-iterated quantities (C, ϕ, γ, δ, etc.) as before. We found AVDEV to be increased by ~0.8, ~0.8, and ~0.4%, respectively. These figures represent a moderately serious deterioration of the fit to the product-ratio data. However, the structural resemblence of 4 and 22 can hardly suffice to fix B precisely as taken in these calculations; values up to 10 times larger or smaller would not be inconceivable. We therefore tried

$$B = 2 \times 10^2 \exp(-10.5/RT) \qquad (2.4\text{-}21)$$

on Calculations 5 and 13, giving Calculations 14 and 15, respectively. The quality-of-fit quantities tabulated in Table 19 shows that under this parameterization the fit to the product-ratio data can even be slightly improved over taking B to be effectively zero.

The reason is not hard to fathom. The effect of allowing hydrogen abstraction by 22 from 1,4-cyclohexadiene to compete with abstraction from cyclohexadienyl radical is (a) to lower the average 1,4-cyclohexadiene concentration and (b) to increase the steady-state cyclohexadienyl radical concentration. Effect (a) increases the systematic errors in the R1 ratios with cyclohexadiene concentration, though not seriously for the revised parameterization of B. But effect (b) counteracts a temperature incompatibility in the R2 ratios which had been accumulating throughout the series of calculations. This incompatibility had $R2^{calc}$ too high for perester **2** runs 1–12, but too low for the perester **1** runs at 99°. Increasing the cyclohexadienyl radical concentration unilaterally for the perester **1** runs makes it possible to form more ring-closed hydrocarbon with the same values of parameters other than B, and hence to reduce the incompatibility.

For the record, we should note something about the actual competition between hydrogen abstraction from 1,4-cyclohexadiene and from cyclohexadienyl radical by **22**. For Calculation 14 (Calculation 15 is similar) the fractions of abstraction events occurring from 1,4-cyclohexadiene were 0.050, 0.084, 0.141, 0.141, and 0.214 for runs 13–17, respectively. For the series at 150° (runs 21–26), the fractions were about half this large. At 0.001 M perester in neat 1,4-cyclohexadiene (runs 36–39), abstraction was largely from 1,4-cyclohexadiene, owing to diminished steady-state radical concentrations.

G. Relation of Quality-of-Fit to Experimental Error

The question of whether deviations between calculated and observed product ratios of the size we have found are compatible with experimental error is fundamental to a judgement regarding the success of the mechanistic treatment at the present level of sophistication. Unfortunately, a definitive answer to this question can not be given.

One reason is that the size of experimental error is difficult to judge. This would usually be done with reference to the repeatability of the observations, but we have tested such reproducibility in too few cases to draw definitive conclusions. Consideration of the reproducibility of repetitive vpc analyses on a given reaction mixture (most runs were analyzed in triplicate) is not a satisfactory substitute. For the record, however, this reproducibility amounts to ~2.5% for the R1 ratios, ~1% for the R2 ratios from perester 2, and ~5% from perester 1.

Several observations suggest that experimental error, arising from uncertainty in reagent concentrations, or from inclusion of variable amounts of adventitious impurities, is larger than considerations of vpc reproducibility alone would indicate. For example, the $R1^{obs}$ from runs 15 and 16, which should be the same, differ by 14%, only about a fifth of which (3%) can be accounted for by the combined scatter in the vpc measurements. Moreover, we have several sets of experiments which lend themselves to examination for consistency. For example, the reduced ratios R, given by % yield 10 x $(ZH)_{av}$/% yield 5, are defined so as to eliminate the large, but really not very interesting, dependence of the product ratio on the cyclohexadiene concentration. As a result, these quantities vary by less than a factor of two. This would suggest that the observed values should vary smoothly as a function of 1,4-cyclohexadiene concentration, reaction temperature, or initial perester concentration. Examination of appropriate reaction series in Table 17 shows that this is not always the case--that real experimental errors must be present.

A second problem is that we do not know precisely how well the data can be fit. If Calculation 15 were to be subjected to optimization of B, C, ϕ, and the parameters describing the solvation effects on E and G, AVDEV, which is 4.4% for Calculation 15, might drop to 4.0%, or perhaps even less.

We believe that Calculation 15 fits the data satisfactorily with few exceptions. However, the same can not be said for Calculations 5 or 14 or for any calculation not involving the ad hoc assumption of solvation effects on E and G. If these effects are real, the fit is satisfactory; otherwise, it is deficient.

If there were precedent for, or independent verification of, solvation effects of the size and type invoked here, we would enthusiastically display Calculation 15 in Table 16 as 'most representative'. Instead, we have chosen Calculation 14 for elaboration of other aspects of the calculations, a number of which are discussed below.

H. Ratio of Rate Constants for Hydrogen Abstraction from 1,4-Cyclohexadiene and ortho-Ring-Cyclization by Ring-opened Radical 3

The rate-constant ratio considered here is E = k_a$/k_r$. From Calculation 14 we find that

k_a$/k_r = 0.050 \exp(0.8/RT)$. (2.4-22)

The reciprocal of eq. 2.4-22 was quoted as eq. 1,8-6, p. 125.

Individual calculations in Table 19 report values which are as much as 0.2 kcal/mole higher and lower than the indicated composite activation energy of -0.8 kcal/mole. In addition, the neglect of any temperature dependence in the conversion efficiency parameters δ and γ could have resulted in overestimation of the true composite activation energy by 0.1–0.2 kcal/mole, if lower temperatures favor radical-radical disportionation over combination as with ethyl radicals (see p. 243); i.e., the true composite activation energy might be -0.9—-1.0 kcal/mole. Moreover, resolution of the temperature incompatibility of the R1 ratios discussed above under heading (1), p. 251, might effect the composite activation energy by 0.5 kcal/mole or more.

Our feeling is that the composite activation energy in eq. 2.4-22 might be incorrect by as much as one kcal/mole.

In contrast, the value of E at 100° (i.e., near the center of the temperature range) seems to be reliably established as 0.145 ± 0.02 M^{-1} sec^{-1}. A major portion of the suggested error limits arises from the average deviation of ~10% between observed and calculated yields of ring-opened hydrocarbon 5, as in Calculation 14 of Table 17.

I. The Characteristic Ratio (6:5) for Hydrogen Abstraction by Ring-opened and Ring-closed Radicals from 1,4-Cyclohexadiene

We previously reported that 1,4-cyclohexadiene develops an impurity upon heating whose retention time closely approximates that of ring-closed hydrocarbon 6 on the standard Ucon polar vpc column (pp. 116 – 118). This most unfortunate coincidence places in doubt our contention that the apparent R2 ratios of ~ 0.004 for 0.001 M ring-opened perester 1 in 1,4-cyclohexadiene (runs 36–39) essentially represent the ratios 6:5 formed via hydrogen abstraction by the (equilibrated) radical precursors from 1,4-cyclohexadiene. However, we found in belatedly measured yields of the solvent-developed impurity reason to believe that the R2 ratios at ~ 0.25 M 1 (runs 13–26) would not be seriously compromised.

We have therefore carried out Calculations 16 and 17 to determine (a) what sort of values of I, the parameter in question, are required to adequately fit the data in the absence of the disputed runs 36–39, and (b) what is the consequence on the quality of the fit of assuming that no 6 is formed via hydrogen abstraction from 1,4-cyclohexadiene, again leaving out runs 36–39. Instead of $I(100^\circ) = 0.0038$ as in Calculation 5, we find, for Calculation 16, $I(100^\circ) = 0.0046$. Although the calculated composite activation energies differ by about 2 kcal/mole, the values for temperatures in the range investigated experimentally agree quite well. In Calculation 17 for $I = 0$, we find AVDEV $R2_1 = 14\%$; comparison to AVDEV $R2_1 = 5.6\%$ for Calculation 5 shows that this parameterization causes a major deterioration in the fit in the only area in which it could be important.

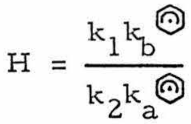
In Calculation 14, which differs from Calculation 5 only in the adoption of eq. 2.4-21 for B, we find $I(100^\circ) = 0.0035$, slightly less than that for Calculation 5. The reason for the reduction is that allowance for hydrogen abstraction by lactonyl radicals 22 from 1,4-cyclohexadiene increases the cyclohexadienyl radical concentration and hence the yield of 6 formed via abstraction of hydrogen from cyclohexadienyl radical. Thus, a smaller fraction of the R2 ratios for runs 36–39 is identifiable with hydrogen abstraction by 4 from 1,4-cyclohexadiene. As values of B could be several times larger than those employed in Calculation 14, I(100°) could be smaller yet. We recommend I(100°) = 0.0035 ± 0.0010 as likely to provide for all contingencies.

The composite activation energy for I specifies, for hydrogen abstraction from 1,4-cyclohexadiene, the energy of the transition state leading to 6 with respect to that leading to 5 (see Fig. 11, p. 119). Consideration of the range of values listed in Table 19 and least-squares standard deviations of ~0.5 kcal/mole obtained according to the formalism given in subsection 2 suggests -1.8 ± 1.0 as a reasonable estimate. We then have

$$I = \frac{k_1 k_b^{\bigcirc}}{k_2 k_a^{\bigcirc}} = 3 \times 10^{-4} \exp(1.8/RT) \quad . \qquad (2.4\text{-}23)$$

J. Characteristic Ratio (6:5) for Hydrogen Abstraction from Cyclohexadienyl Radical

The characteristic ratio 6:5 for hydrogen abstraction from cyclohexadienyl radicals is of interest for comparison to values already obtained for 1,4-cyclohexadiene (~0.0035 at 100°) and for triethyltin hydride (~0.07 at 100°; see p. 168). From eq. 1.8-12 (p. 138) we know that hydrogen abstraction by 3 is more rapid from triethyltin hydride than from 1,4-cyclohexadiene by a factor of ~50 at 100°. Thus, more use of the active hydrogen donor corresponds to larger **6**:**5**. As cyclohexadienyl radicals should be vastly more reactive than either of these toward the relatively stable dibenzylic ring-closed radical, a much larger characteristic ratio is to be expected. Indeed, the Calculations indicate that the ratio, given by the parameter H, is so large that



$$H = \frac{k_1 k_b^{\odot}}{k_2 k_a^{\odot}} \qquad (2.4\text{-}24)$$

formation of ring-opened hydrocarbon by this pathway is all but undetectable. In Calculation 5 we find H(100°) = 5.6. In Calculation 14 (where the revised parameterization for B, eq. 2.4-21, is employed), we find H(100°) = 20. With solvation corrections to E and $\dot{G}$, (Calculation 13) we have H(100°) = 14. With revised parameterization for B (Calculation 15), the computer was given H(100°) = 50, found that to be too small, increased it to 220, thence to 4800, and finally to 10^{121}.

Even for Calculation 5, which had H(100°) = 5.6, formation of **5** via hydrogen abstraction from cyclohexadienyl radical was not crucial to the success of the fit. This was shown in Calculation 18 where we assumed H(100°) = 10^{10} (i.e., effectively infinite); AVDEV rose by only 0.14% over that for Calculation 5.

The conclusion is that H(100°) is greater than unity, but by an amount which can not be reliably determined with the present data. It is probably safe to recommend H(100°) ≥ 5.

K. Enthalpy Difference of Ring-opened Radical 3 and Ring-closed Radical 4

Values of H quoted above were determined for the composite activation energy for H of -8 kcal/mole. As the activation energies of the $k_a^{\odot}$ and $k_b^{\odot}$ processes of eq. 2.4-24 may be expected to be both small and similar, the composite activation energy for H may reasonably be equated to the difference in enthalpy of the ring-closed and ring-opened radicals.

From eqs. 2.1-4 we find that

$$\frac{G^{*}k_4^{\frac{1}{2}}}{E^{*}F^{\frac{1}{2}}} = \frac{k_1 k_b^{\odot}}{k_2 k_a^{⬡}} \quad . \tag{2.4-25}$$

The composite activation energy of this quantity specifies the difference in energy between the transition state for formation of 6 via abstraction of hydrogen by 4 from cyclohexadienyl radical and the transition state for formation of 5 from 3 plus 1,4-cyclohexadiene. If we employ the numerical results for Calculation 14 (Table 19) and assume a viscosity-related activation energy of 2 kcal/mole for k_4, the rate constant for pairwise reaction of cyclohexadienyl radicals, we find this energy difference to be -13.35 -1.00 - (-0.77) = -11.6 kcal/mole. A survey of other calculations in Table 19 shows that the last figure is remarkably insensitive to the precise assumptions of the least-squares optimization.

If the activation energy for abstraction of hydrogen by ring-opened radical 3 from 1,4-cyclohexadiene is assumed to be 5.8 kcal/mole (see p. 108), and if that for the reaction of **4** with cyclohexadienyl radical is taken to be 2 kcal/mole, we have that the enthalpy of ring-closed radical **4** is lower than that of **3** by 11.6 - 5.8 + 2.0 $\cong$ 8 kcal/mole. These relationships are traced in Fig. 22.

Uncertainty in various assumptions make the enthalpy difference uncertain by perhaps 3 kcal/mole. Firstly, the 5.8 kcal/mole activation energy for the k_a  reaction assumes (a) that ring-opened radicals and ethyl radicals are equally reactive toward 1,4-cyclohexadiene; (b) that the activation energy is not effected by transferring the model ethyl radical system from the gas phase into hydrocarbon solution; and (c) that bimolecular reaction of ethyl radicals requires no activation energy (see p. 108). In addition, the viscosity-related activation energies for the k_4 and k_b  processes might differ by 1—2 kcal/mole from the values of 2 kcal/mole assumed here. However, a consistent error here would come in only at half strength because k_1/k_2 depends on $k_4^{\frac{1}{2}}/k_b$ . Finally, the R2 ratios depend essentially on the product $G^*k_o^{\frac{1}{2}}$, where k_o denotes the rate constant for perester decomposition; an error of 1 kcal/mole in the assumed enthalpy of activation of 24.5 kcal/mole for decomposition of **2** would effect k_1/k_2 by 0.5 kcal/mole.

If the classical radicals are really the intermediates, the figure of 8 ± 3 kcal/mole should be compatible with expectations based on bond energies and the like. We shall show in Section Three via a thermochemical cycle, itself subject to sizable uncertainties, that such is evidently the case.

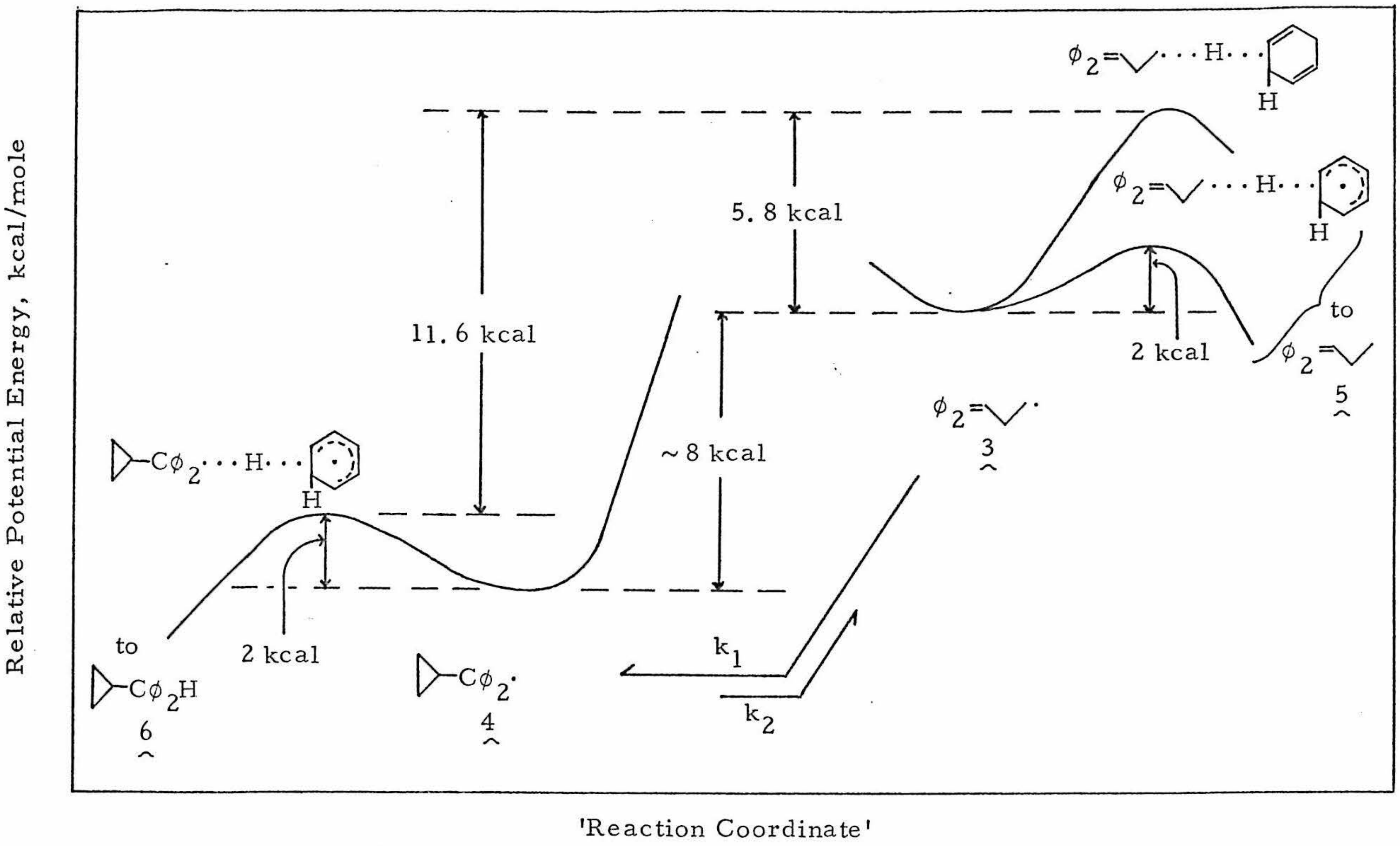


Figure 22. Reaction diagram showing derivation of enthalpy difference (~8 kcal/mole) between ring-opened radical 3 and ring-closed radical 4.

L. Self- and Cross-termination of Ring-cyclized Radicals and Cyclohexadienyl Radicals

The parameter $F = k_3k_4/k_d^2$ measures the competition between self- and cross-termination in a system containing ring-cyclized radicals and cyclohexadienyl radicals. The value of F expected statistically (i.e., if collisions of 9 with 9, 9 with cyclohexadienyl radical, and of cyclohexadienyl with cyclohexadienyl are equally effective) is 0.25(100). Values found in these calculations range from 0.056 to 0.082. Thus, cross-termination appears to be favored over self-termination by approximately a factor of $(0.25/0.07)^{\frac{1}{2}} \cong 2$. No such bias exists for simple alkyl radicals in the gas phase (109). For electronically dissimilar radicals (i.e., one an electron donor, the other an electron acceptor), cross-termination is favored by factors up to 150(110), but as 9 is a substituted cyclohexadienyl radical, this sort of explanation would not seem to be applicable. Perhaps steric factors are responsible. In any case, the deviation from the statistically expected result is not very large.

In calculations heretofore reported, we have assumed a composite activation energy for F of zero kcal/mole. As the k_3, k_4 and k_d processes may well all be diffusion-controlled, this assumption is not unreasonable. Moreover, from the way in which F is formed from these rate constants, we would expect, even if more than the usual diffusion-controlled activation energies are involved, that the sum of the activation energies for k_3 and k_4 would closely approximate twice that for k_d.

Calculations 19 and 20 explore the consequences of taking the composite activation energy for F to be ± 1 kcal/mole. The quality-of-fit quantities listed in Table 19 show that the assumed value of zero (Calculation 5) is superior to either ± 1, but only marginally so for + 1. Indeed, values other than zero principally affect not the quality of the fit but the values found for the other parameters, though not very strongly except for the composite activation energy for G. Interestingly, the variation for G is just such as to leave the estimated difference in enthalpy of the radicals **3** and **4** unchanged to within 0.1 kcal/mole.

M. Yields of Tetrahydronaphthalene (**B**)

Columns 2 and 3 of Table 17, p. 298, give calculated and, where available,* observed yields of **B** (see Chart 4, p. 78) for Calculation 14, where we have used $\gamma = 0.60$, $\delta = 0.42$, and $\epsilon = 0.28$. The value $\gamma = 0.60$ implies that 30% of ring-cyclized radicals which react pairwise come out as tetrahydronaphthalene. Similarly, $\epsilon = 0.28$ means that reaction of **9** with cyclohexadienyl radical involves transfer of a hydrogen atom to **9** some 28% of the time. These values correctly predict yields of **B** in an average sense.

Comparison of observed and calculated yields in Table 17 shows that the variation with cyclohexadiene concentration is also predicted approximately correctly. Of course, a variety of mechanisms for

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*See the footnote to p. 241.

destruction of **B** (e.g., Diels-Adler reaction with 1,4-cyclohexadiene, attack by radical intermediates) can be invoked to explain the rather erratic behavior of the observed yields as a function of the 1,4-cyclohexadiene concentration.

N. Formation of Dimers from Ring-cyclized Radicals

If reactions of ring-cyclized radicals with themselves or with cyclohexadienyl radicals do not always result in disproportionation, dimers containing the C_{16} moiety will be formed. Predicted yields for $\gamma = 0.60$, $\delta = 0.42$, and $\epsilon = 0.28$ appear in Table 17, p. 298. The average yield of 'missing C_{16} groups' is 11% for runs employing ring-opened perester **1** and 8% for runs employing **2**. The last of these quantities essentially explains the material balance deficit of approximately 10% for runs employing **2** (pp. 122,123). However, the average calculated yield for runs employing **1** accounts for only about half the observed material balance deficit of ~20%. The remaining deficit of ~10%, might be attributable to induced decomposition of **1** by cyclohexadienyl radicals; this would principally affect yields of **5**, **6**, and **10**, but would leave their ratios all but invariant.

O. Formation of Dimers from Cyclohexadienyl Radicals

We consistently observed a product (not biphenyl) at approximately one-fifth the retention time of ring-opened hydrocarbon **5** on the standard Ucon polar column. This product appeared upon decomposition in 1,4-cyclohexadiene of ring-opened perester **1**, ring-closed perester **2**, or saturated perester 8. In no other solvent was similar material observed. Largely on this basis, the material was assumed to result from coupling of cyclohexadienyl radicals. No attempt was made either to determine whether the observed vpc peak might be due to more than a single material (111) or to isolate and characterize the material.

However, peak areas were generally monitored. Yields calculated assuming unexceptional vpc response characteristics for the dimer are displayed in Tables 1, 2, and 3. The yields, it may be seen, increase with increasing 1,4-cyclohexadiene concentration, but not proportionately.

In terms of the present reaction mechanism, we can write

$$\text{mM cyclohexadienyl radical dimer/mM perester taken} =$$

$$\frac{1}{2(P)_o} \int_0^\infty 2\xi k_4 (Z\cdot)^2 \, dt \quad , \qquad (2.4\text{-}26)$$

where ξ is the fraction of pairwise reactions resulting in formation of the dimer. Using the usual exponential relationship for first-order decomposition between perester concentration and time, as in Appendix B, the definitions of F (eq. 2.1-4) and X (eq. 2.1-8), we can rewrite eq. 2.4-26 in the form

$$\text{mM dimer/mM perester} = \xi\alpha \int_0^1 \frac{F}{2X} \, dz \quad , \qquad (2.4\text{-}27)$$

where α is the fraction of perester decompositions yielding either 3 or 4 and $z \equiv (P)/(P_o)$ is the variable of integration, as in eqs. 2.1-1— 2.1-3.

Yields of dimer calculated from eq. 2.4-27 using the standard three-point Gaussian quadrature (Appendix B) are displayed for Calculation 14 in Table 17, p. 298, alongside the observed quantities. The calculated yields employ values of α taken from a neighboring column of Table 17 together with $\xi = 0.40$.

Comparison of observed and calculated quantities reveals that yields are underestimated for runs employing perester **2**, but overestimated for runs employing **1**. Indeed, if ξ is evaluated for each run so as to produce agreement between the observed and calculated yields, one finds $\xi = 0.38 \pm 0.08$ for all runs, but 0.45 ± 0.05 for runs employing **2** and 0.32 ± 0.04 for runs employing **1**. Thus, the data are not as unmindful of the identity of the starting perester as one might like.

Several considerations may be advanced to account for the roughness of the fit. The lower apparent values of ξ at higher reaction temperatures might indicate that higher temperatures favor disproportionation over combination. Destruction of dimer via radical attack at $\sim$1 M 1,4-cyclohexadiene and via Diels-Alder addition to 1,4-cyclohexadiene at higher cyclohexadiene concentrations could also be important. Moreover, the appearance of the vpc peak of the dimer on the tail of the solvent peak and an observed sensitivity of peak areas to injector temperatures combine to ensure that the quality of the data is low. Radical-induced decomposition via attack of cyclohexadienyl radicals on ring-opened perester **1** would serve to selectively lower yields of the radical dimer at higher cyclohexadiene concentrations.

Finally, the radical dimer might redissociate to cyclohexadienyl radicals (and thus feed over to disproportionation products) on the time scale of the perester decompositions when the starting perester is 1, but not when it is 2. This is not unreasonable because comparable reaction times for ten perester-decomposition half-lives requires a reaction temperature for perester 1 roughly 100° higher than that for perester 2. The comparison of observed and calculated yields of the dimer indicates that some redissociation may have occurred, but can not be rapid on the perester-decomposition time scale.

This is an important point, for we have made no mechanistic provision for the possibility that dimer containing the ring-cyclized moiety might similarly redissociate. Occurrence of the latter would cause the effective values of the conversion efficiency parameters γ and δ to increase abruptly on going from 70° for perester 2 to 99° for perester 1. Assumption of such behavior would unilaterally decrease $R1^{calc}$ at 99—150°. However, the $R1_c^{calc}$ already tend to be too low at 99° but too high at 70°; inclusion of redissociation would increase the temperature incompatibility in the R1 ratios discussed under heading (1), p. 251.

Our conclusion is that the coupling products from cyclohexadienyl and ring-cyclized radicals do not rapidly redissociate on the time scale of the perester decompositions.

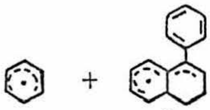
James and Suart report (52) that the fraction of pairwise reactions of cyclohexadienyl radicals in the gas phase at 23—117° which result in coupling rather than disproportionation is 0.69. Our estimate for a similar temperature range in hydrocarbon solution is

$\xi = 0.40$. It is interesting in this connection that the ratio of disproportionation to combination for ethyl radicals at 0° is 0.13 in the gas phase but 0.18 in isooctane solution (103). Our data may confirm the suggestion (103) that solvent cages (or simply the condensed phase) favor disproportionation over combination.

P. Summary of Interactions of Ring-cyclized Radicals and Cyclohexadienyl Radicals

We now have available information concerning the patterns of coupling and disproportionation for 9 with 9, 9 with cyclohexadienyl, and cyclohexadienyl with cyclohexadienyl. We have recorded this information in Table 16 with a view to providing a possible measure of the consistency of the various assumptions and observations.

Table 16. Probabilities of Disproportionation and Combination for Pair-wise Reactions of Two Cyclohexadienyl-type Radicals.

Reactants	Probability of disproportionation	Probability of coupling
	0.6	0.4[a]
 9	0.7[b]	0.3
9 + 9	0.6–0.7[c]	0.3–0.4

[a] Evaluated from observed yields of cyclohexadienyl radical dimer.

[b] Made up of $\delta = 0.42$ (required to fit yields of 5) and $\epsilon = 0.28$ (required to fit yields of tetrahydronaphthalenes B); see Chart 7, p. 198 for definitions of δ and ϵ.

[c] Required to account for yields of dihydronaphthalene 10 for reaction of 1 in triethyltin hydride; see the discussion on pp. 260 – 261.

Cyclohexadienyl radicals and ring-cyclized radicals apparently behave rather similarly. In view of their structural kinship, this is perhaps not surprising. We previously noted that the ratio data in 1,4-cyclohexadiene could be fit better if we assumed that pairwise reaction of ring-cyclized radicals nearly always results in dimerization (Calculation 11, Tables 18, 19). While footnote c above may suffice to reject that parameterization, we can perhaps add here that the structural kinship of cyclohexadienyl radical and **9** would make it difficult to understand why the two cases (rows 1 and 3 in Table 16) should be greatly different.

Q. Extent of Reversibility of the Ring-cyclization Process

Evidence for reversibility of the *ortho*-ring cyclization process (the k_{-r} process of Chart 7, p. 198) should show up most strongly as systematically low predictions for R1 ratios at low initial perester concentrations and high reaction temperatures. Runs 35–38 (initial perester concentrations, 0.001 M; reaction temperatures, 99–125°) best meet these experimental prerequisites. The RELDEV R1 quantities for these runs in Calculation 5 (see Table 18, p. 300) range from -8.5% to -18.6%. Although the calculated ratios are indeed systematically low, it is clear that decyclization can not be very important even under these conditions.

We should perhaps recall here that these runs, and several others at low initial perester concentrations, were not included in the optimization procedure so that comparison of observed ratios to (calculated) ratios in effect extrapolated from measurements at higher perester concentrations could be used to judge the importance of the decyclization process.

A series of calculations were carried out to establish the maximum value for the decyclization parameter $D = k_{-4}/k_3^{\frac{1}{2}}$ compatible with the data. This was done by taking all other parameters as in Calculation 5 while gradually 'turning on' the decyclization and observing the result on the RELDEV R1 quantities for runs 35–38. For these calculations we have assumed a composite activation energy for D of 18 kcal/mole (see below) and have varied the composite preexponential factor. A preexponential factor of 10^6 raised the average RELDEV R1 for the four runs from -12% to zero, while 2×10^6 gave an average RELDEV R1 of +10%. We can therefore take 2×10^6 to be the maximum value allowed for the data.

Using the assumed 18 kcal/mole composite activation energy, this gives $D(100^\circ) \leq 5 \times 10^{-5}$ (liter-sec/mole)$^{-\frac{1}{2}}$. If we further assume $k_3 = 4 \times 10^9 \exp(-2/RT)$ (this gives $k_3 \cong 3 \times 10^8$ sec^{-1} at 100°), we obtain

$$k_{-r} \quad 10^{10} \exp(-19/RT) \quad (M^{-1} \sec^{-1}) \quad . \tag{2.4-28}$$

For purposes of comparison, we shall record here the estimate (p. 349) for the <u>ortho</u>-ring-cyclization rate constant:

$$k_r = 4 \times 10^{10} \exp(-6.6/RT) \quad (M^{-1} \sec^{-1}) \quad . \tag{2.4-29}$$

The ratio k_{-r}/k_r, gives the equilibrium constant for the radicals 3 and 9. If, then, the entropies of the radicals are not greatly different, the preexponential factor for k_{-r} would appear to be reasonable.

Eqs. 2.4-28 and 2.4-29 state that the ring-cyclized radical 9 lies lower in enthalpy than the ring-opened radical 3 by ~ 12 kcal/mole. Our prediction that this should be the case was the basis for taking the composite activation energy for D to be 18 kcal/mole. The experimental result we start with is the report by James and Suart that addition of a hydrogen atom to benzene is exothermic by 27 kcal/mole (52). If we can estimate from this the exothermicity for addition of an ethyl radical to benzene, we will have a reasonable model for the <u>ortho</u>-ring-cyclization process.

Walling notes that the C–H bond dissociation energy for ethane, the energy required to dissociate molecular hydrogen, and heats of formation of ethane and ethylene can be employed in a thermochemical cycle to calculate a value of 40 kcal/mole for the energy required to dissociate a β-hydrogen atom from the ethyl radical (112). Using an analogous cycle starting from butane instead of ethane, assuming that the dissociation energy of a primary C–H bond in butane is the same as in ethane, and taking heats of formation from standard tables (113), one can calculate $D(Et{-}CH_2CH_2\cdot) = 22$ kcal/mole. Thus, addition of an ethyl radical to ethylene is less exothermic than addition of a hydrogen atom by ~ 18 kcal/mole.

A similar comparison indicates that addition of an ethyl radical to butadiene is less exothermic than addition of a hydrogen atom by ~16 kcal/mole.

On this basis, we estimate that addition of an ethyl radical to benzene should be exothermic by 27 - 17 = 10 kcal/mole. This figure is most appropriate for the cyclization of saturated radical 21 to 24, as the latter is an alkyl-substituted cyclohexadienyl radical. Greater exothermicity would be expected for ring-cyclization by 3 because of the more extensive π-system which results. We can estimate from the localization energy considerations of pp. 145–149 that this factor should be 'worth' about 2 kcal/mole, so that ring-cyclization by 3 should be exothermic by ~ 12 kcal/mole.

These considerations neglect any specifically conformational contributions to the relative energies of 3 and 9. However, such factors could well be small.

In contrast, we have previously estimated isomerization of 3 to 4 to be exothermic by 8 ± 3 kcal/mole. In addition, opening of the strained three-membered ring for 4 → 3 may well carry a higher frequency factor than opening of a six-membered ring for 9 → 3. The net result is that the former process is rapidly reversible, but the latter effectively irreversible, under conditions studied.

R. Summary of the Mechanistic Conclusions

The mechanistic scheme of Chart 7, p. 198, gives an average relative deviation of 6.1% between calculated and observed product ratios R1 and R2, where R1 ≡ % yield 5/% yield 10 and R2 ≡ % yield 6/% yield 5. Examination of the success of the basic fit (Calculation 1, Table 18 (p. 299)) on a run-by-run basis reveals the presence of several types of systematic errors--subtleties in the product-ratio data which are not reproduced in the calculated quantities.

Sizable systematic errors of two types could be eliminated, but only upon modification of the mechanistic scheme. The first of these consisted in a strong tendency for calculated values of R2 to deviate positively at low 1,4-cyclohexadiene concentrations and negatively at high concentrations. It was shown that the mechanistic inadequacy could not be attributed to failure of the assumption of rapid reversibility of ring-closed radical **4** with ring-opened radical **3** (heading (a), p. 252). A solvent effect on the rate constants for perester decomposition could in principle be responsible, but was not invoked. It proved possible to eliminate the systematic deviations by taking the rate constants for radical-radical processes, specifically for reaction of ring-closed radical **4** with cyclohexadienyl radical (rate constant $k_b^{\odot}$), to be proportional to the reciprocal of the solvent viscosity, as is suggested by theoretical treatments based on models of the liquid phase (e.g., eq. 2.4-7, p. 255). This subject is discussed under heading (d), p. 254. Viscosities of 1,4-cyclohexadiene--cyclohexane mixtures were measured at 20°; the variation was found to account nicely for the size and nature of the systematic deviations in R2 (Calculation 5, p. 300).

The calculated R1 ratios were found to exhibit negative deviations at low 1,4-cyclohexadiene concentrations and positive deviations at high cyclohexadiene concentrations (heading (3), p. 259). A possible explanation--that inadequate allowance was made for variation of the efficiency with which ring-cyclized radicals **9** are converted to the dihydronaphthalene **10** as a function of reaction conditions--was shown to fail; Calculation 11 (Table 18, p. 300) employed the maximum of variability of conversion efficiency attainable in our mechanistic scheme, but was unable to significantly reduce the scope of the especially severe systematic deviations for runs employing ring-closed perester 2.

It was then necessary to assume that the rate-constant ratio E = k_a$/k_r$, which controls the partitioning between formation of 5 via hydrogen abstraction and ring-cyclization to 9, is a function of the solvent composition (eq. 2.4-15, p. 263). As with the *t*-butoxy radical (42), complexing solvents (such as the olefinic 1,4-cyclohexadiene) appear to favor a unimolecular process over bimolecular hydrogen abstraction, perhaps by partial exclusion of the hydrogen donor from the neighborhood of the radical center by association of the latter with solvent. Elimination of the systematic deviations in the R1 ratios required the assumption that E decreases by ~30% at 0° and ~15% at 150° on going from pure cyclohexane as solvent to pure 1,4-cyclohexadiene. It was possible to reduce the average deviation for R1 ratios where the starting perester is 2 from 10-11% to < 6% (Calculations 12, 13, and 15, Table 18) and, with some further modifications, to reduce the overall average deviation from 5.8% (Calculation 5) to 4.4% (Calculation 15).

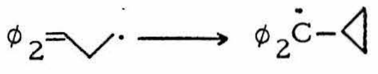
Although solvation effects of even the small magnitude tentatively inferred here seem not to have been previously implicated for reactions of nonpolar hydrocarbon radicals (perhaps simply due to lack of investigation), the resultant improvement in the quality of the fit is sufficiently large to suggest that the assumed effects are real. It appears to be feasible to obtain experimental verification of the assumed medium effects, both regarding the partitioning between hydrogen abstraction and ring-cyclization and the theoretically better justified effect of viscosity on the rates of radical-radical processes (heading E, p. 266).

The rate constant ratio $k_a^{\text{⌬}}/k_r$ is found to be 0.145 ± 0.02 at 100° (heading H, p. 272). As we previously had $k_a^{\mathrm{SnH}}/k_r \cong 7$ at the same temperature, we conclude that abstraction of hydrogen by ring-opened radicals **3** is more rapid from triethyltin hydride than from 1,4-cyclohexadiene by a factor of ~50 at 100°.

Certain experiments at low initial concentrations of ring-opened perester **1** (0.001 M) seem to give directly the relative amounts of ring-closed hydrocarbon **6** and ring-opened hydrocarbon **5** formed via abstraction of hydrogen from 1,4-cyclohexadiene. However, the experimental validity of these experiments is clouded by the observation that 1,4-cyclohexadiene itself develops one or more impurities which would be mistaken for **6** upon routine vpc analysis. It was shown (a) that the fit to the product ratios at much higher initial perester concentrations (~0.25 M) determines much the same value for the parameter I, the quantity in question (Calculation 16) and (b) that assuming no **6** is formed by hydrogen abstraction from 1,4-cyclohexadiene raises the average deviation for product ratio R2 from 5.6% (Calculation 5) to 14% (Calculation 17) for higher perester concentration runs starting from ring-opened perester **1**. We concluded, not entirely without reservations, that hydrogen abstraction from 1,4-cyclohexadiene gives characteristic ratio **6**:**5** of 0.0035 ± 0.0010 at 100° (heading I, p. 273). The analogous quantity for abstraction from triethyltin hydride is ~0.07, indicating that whereas ring-opened radical **3** abstracts hydrogen from the tin hydride ~50 times more rapidly than from 1,4-cyclohexadiene (see above), ring-closed radical 4 prefers the tin hydride by a factor of ~1000.

In contrast, hydrogen abstraction from the very reactive cyclohexadienyl radical appears to yield 6 and 5 in the ratio of at least 5:1 at 100° (heading J, p. 275).

It was possible to estimate reasonably directly that isomerization of ring-opened radical 3 to ring-closed radical 4 is exothermic by 8 ± 3 kcal/mole (heading K, p. 277).



3 4

$\Delta H_{isom} = -8 \pm 3$ kcal/mole

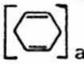
Dihydronaphthalene 10 accounts for only about 40% of precursor ring-cyclized radicals 9. The remaining 60% presumably appear as tetrahydronaphthalenes, resulting from addition of a hydrogen atom to 9, or as radical-radical coupling products. Calculated yields of tetrahydronaphthalene correlate reasonably well with observed yields of a substance tentatively assigned that identity (heading M, p. 281). Calculated yields of dimer then account nearly quantitatively for the 10% material balance deficit for observed monomeric products for reactions of ring-closed perester 2, but for only half of the 20% deficit for reactions of ring-opened 1. Radical-induced decomposition of 1 by cyclohexadienyl radicals may play a minor role (heading N, p. 282).

Calculated yields of coupling product from cyclohexadienyl radicals correlate roughly with observed yields. The fraction of pairwise reactions resulting in coupling rather than disproportionation is ~0.4, compared to a report of 0.7 in the gas phase (52). It appears that the radical dimers from coupling of cyclohexadienyl radicals or ring-cyclized radicals (which are substituted cyclohexadienyl radicals) redissociate at best slowly at 100° hrs (heading O, p. 282).

The competition between coupling and disproportionation appears to be similar for pairwise reaction of cyclohexadienyl radicals or of ring-cyclized radicals or for reaction of ring-cyclized radicals with cyclohexadienyl radicals (heading P, p. 286).

The decyclization of ring-cyclized 9 to ring-opened 3 competes at best inefficiently with consumption of 9 in radical-radical reactions even for 0.001 M ring-opened perester at 100–150°. This is shown to be consistent with estimates for the heat of isomerization for cyclization of 3 to 9 and for the rate of the forward process (heading Q, p. 287).

Table 17. Least-Squares Calculation No. 14[a] for Decomposition of Peresters 1 and 2 in Solutions of 1, 4-Cyclohexadiene in Cyclohexane.

RUN	Bath Temp. °C	Per-ester Iden-tity	Initial Perester Conc. M	 av[b] M	$R1^{obs}$[c]	$R1^{calc}$[c]	RELDEV[d] R1	RWT1[e]
1	0	2	0.050	2.94	1.57	1.35	-14.0	0.899
2				5.31	2.68	2.49	- 7.3	0.960
3				7.96	3.51	3.77	7.3	0.974
4				10.79	4.49	5.16	14.9	0.981
5	35	2	0.050	2.81	1.35	1.11	-17.5	0.900
6				5.09	2.28	2.04	-10.4	0.961
7				7.63	2.91	3.09	6.2	0.974
8				10.36	4.08	4.23	3.7	0.985
9	70	2	0.050	2.70	0.97	0.96	- 1.0	0.856
10				4.88	1.62	1.75	7.8	0.940
11				7.32	2.48	2.63	6.2	0.968
12				9.93	2.82	3.59	27.4	0.964
13	99	1	0.265	0.90	0.45	0.33	-26.5	0.402
14				1.82	0.75	0.66	-12.6	0.660
15				4.06	1.64	1.44	-12.4	0.904
16				4.06	1.42	1.44	1.1	0.876
17				8.28	2.92	2.89	- 1.0	0.966
18	131	1	0.260	0.91	0.36	0.31	-13.7	0.334
19				1.81	0.66	0.61	- 8.1	0.638
20				3.99	1.33	1.31	- 1.3	0.881
21				8.10	2.58	2.62	1.6	0.964
22	150	1	0.255	0.91	0.33	0.30	- 8.5	0.311
23				1.78	0.58	0.58	0.7	0.592
24				3.92	1.24	1.26	1.3	0.873
25				7.96	2.34	2.51	7.1	0.960
26				7.96	2.33	2.51	7.5	0.960
27	35	2	0.101	2.42	1.14	0.91	-19.9	0.851
28			0.0220	2.51	1.09	1.03	- 5.5	0.862
29			0.0060	2.53	1.21	1.08	-10.9	0.
30			0.0010	2.53	1.11	1.11	0.1	0.
31	110	1	0.270	0.92	0.38	0.33	-13.6	0.332
32			0.030	1.20	0.43	0.42	- 1.9	0.
33			0.030	1.20	0.43	0.42	- 1.9	0.
34			0.0051	1.23	0.44	0.43	- 2.9	0.
35			0.0010	1.23	0.50	0.42	-15.1	0.
36	99	1	0.0010	9.65	4.1	3.34	-18.5	0.
37	110		0.0010	9.45	3.5	3.17	- 9.4	0.
38	125		0.0010	9.34	3.3	3.03	- 8.1	0.
39	144		0.0010	9.20	---	2.87	---	0.

[a] See Table 19 for values of parameters and quality-of-fit quantities.

[b] See Tables 1, 2, 4, 5, and 6 for initial concentrations.

[c] % yield 5/% yield 10. [d] (calc−obs)/obs x 100%.

[e] Relative weight; see eq. 2.4-2; for explanation of zero values, see pp. 242, 247.

Table 17 (cont.)

RUN	Reduced Ratio[f] R OBSVD	 CALC	R2obs[g]	R2calc[g]	RELDEV[d] R2	RWT2[h]	% Yield 5[i] OBSVD	 CALC
1	1.87	2.17	0.715	0.770	7.7	2.00	18.9	19.8
2	1.98	2.14	0.487	0.514	5.6	2.43	26.5	28.2
3	2.27	2.11	0.392	0.396	1.1	2.60	33.7	35.1
4	2.40	2.09	0.335	0.320	-4.3	2.68	38.5	40.9
5	2.08	2.53	0.769	0.797	3.6	2.05	22.1	19.4
6	2.23	2.49	0.518	0.526	1.5	2.48	31.1	28.3
7	2.62	2.47	0.400	0.402	0.5	2.62	35.5	35.7
8	2.54	2.45	0.325	0.324	-0.4	2.68	45.0	41.9
9	2.79	2.82	0.763	0.814	6.7	1.72	19.8	18.7
10	3.01	2.80	0.540	0.534	-1.1	2.22	29.6	27.7
11	2.95	2.78	0.405	0.407	0.4	2.39	35.8	35.3
12	3.52	2.76	0.349	0.327	-6.2	2.54	37.0	41.8
13	2.01	2.73	0.033	0.033	0.2	0.25	9.0	7.5
14	2.42	2.77	0.020	0.021	3.2	0.38	11.8	13.7
15	2.48	2.83	0.013	0.013	1.9	0.43	20.6	24.6
16	2.86	2.83	0.013	0.013	1.9	0.43	19.7	24.6
17	2.83	2.86	0.010	0.010	-4.3	0.44	28.6	37.4
18	2.53	2.93	0.052	0.051	-2.4	0.24	9.5	7.6
19	2.74	2.98	0.028	0.030	7.8	0.36	14.4	13.9
20	3.00	3.04	0.017	0.018	6.3	0.42	22.2	25.2
21	3.14	3.09	0.011	0.012	10.5	0.44	30.4	38.7
22	2.74	3.00	0.051	0.059	16.3	0.20	8.1	7.4
23	3.07	3.05	0.034	0.035	3.0	0.36	13.7	13.4
24	3.16	3.12	0.020	0.021	3.0	0.42	21.7	24.4
25	3.40	3.18	0.013	0.014	4.2	0.44	31.3	37.8
26	3.41	3.18	---	0.014	--	0.	31.5	37.8
27	2.12	2.65	1.17	1.215	3.9	1.73	17.9	16.2
28	2.31	2.44	0.640	0.600	-6.2	2.13	22.0	19.2
29	2.09	2.34	0.350	0.329	-6.1	2.19	28.5	20.7
30	2.28	2.28	0.165	0.142	-13.9	2.30	26.9	21.8
31	2.42	2.80	0.044	0.038	-14.3	0.	6.7	7.4
32	2.79	2.84	0.020	0.013	-32.6	0.	9.7	9.3
33	2.79	2.84	0.021	0.013	-35.8	0.	9.5	9.3
34	2.79	2.87	0.012	0.008	-33.7	0.	8.2	9.5
35	2.46	2.90	0.011	0.006	-48.6	0.	9.9	9.5
36	2.35	2.89	0.0040	0.0040	0.3	0.99	--	40.1
37	2.70	2.98	0.0036	0.0038	6.2	0.99	--	40.3
38	2.83	3.08	0.0038	0.0037	-3.8	1.00	--	41.7
39	--	3.21	0.0037	0.0035	-5.6	1.00	--	40.6

[f] % yield 10 x $(⌬)_{av}$/% yield 5. [g] % yield 6/% yield 5.

[h] Analogous to RWT1[e]; for explanation of zero values, see pp. 247, 266.

[i] Average deviation between calculated and observed yields ≅ 10%.

Table 17 (cont.)

RUN	% Yield[j] Tetrahydronaphthalene(s) OBSVD	% Yield[j] Tetrahydronaphthalene(s) CALC	% Yield[k] Dimer from 9 CALC	% Yield[l] Cyclohexadienyl-Radical Dimer OBSVD	% Yield[l] Cyclohexadienyl-Radical Dimer CALC	Fraction[m] Radical Pairs (≡ α)	Average Value[n] W	Average Value[n] X
1	--	6.9	7.6	0.10	0.09	0.67	0.48	0.097
2	--	5.2	5.7	0.13	0.12	0.68	0.37	0.075
3	---	4.2	4.6	0.16	0.15	0.70	0.30	0.064
4	--	3.6	3.9	0.19	0.17	0.72	0.25	0.057
5	--	8.2	9.1	0.12	0.09	0.73	0.52	0.104
6	--	6.4	7.0	0.15	0.12	0.74	0.42	0.080
7	--	5.3	5.8	0.16	0.15	0.76	0.34	0.068
8	--	4.5	4.9	--	0.17	0.78	0.29	0.060
9	--	9.3	10.3	0.12	0.09	0.77	0.56	0.110
10	--	7.4	8.1	0.16	0.12	0.78	0.46	0.085
11	--	6.2	6.7	0.13	0.15	0.80	0.38	0.072
12	--	5.3	5.8	0.15	0.17	0.82	0.32	0.063
13	9.7	11.0	12.4	0.06	0.08	0.65	0.88	0.108
14	7.6	9.9	11.1	0.09	0.11	0.66	0.79	0.078
15	8.2	8.0	8.8	0.12	0.18	0.67	0.63	0.051
16	8.4	8.0	8.8	0.11	0.18	0.67	0.63	0.051
17	5.8	5.9	6.4	0.14	0.26	0.69	0.45	0.036
18	13.6	12.1	13.9	0.08	0.07	0.71	0.89	0.131
19	12.1	11.1	12.5	0.09	0.09	0.72	0.80	0.101
20	10.7	9.0	10.0	0.13	0.14	0.73	0.65	0.069
21	9.5	6.8	7.4	0.17	0.20	0.75	0.48	0.049
22	12.2	12.2	13.9	0.06	0.07	0.71	0.89	0.137
23	15.6	11.2	12.6	0.07	0.09	0.72	0.81	0.107
24	11.5	9.2	10.2	0.10	0.13	0.73	0.66	0.074
25	8.4	7.0	7.6	0.14	0.19	0.75	0.49	0.053
26	10.0	7.0	7.6	--	0.19	0.75	0.49	0.053
27	7.1	8.4	9.4	--	0.08	0.73	0.51	0.117
28	7.1	8.8	9.8	--	0.09	0.73	0.58	0.102
29	6.5	9.1	10.2	--	0.10	0.73	0.62	0.097
30	5.9	9.4	10.5	--	0.11	0.73	0.66	0.092
31	5.5	11.0	12.5	--	0.07	0.65	0.88	0.117
32	13.4	10.6	11.9	--	0.11	0.65	0.85	0.081
33	12.3	10.6	11.9	--	0.11	0.65	0.85	0.081
34	11.9	10.6	11.7	--	0.15	0.65	0.85	0.060
35	13.1	10.5	11.6	--	0.20	0.65	0.85	0.045
36	--	5.5	5.9	--	0.55	0.69	0.42	0.017
37	--	5.8	6.3	--	0.48	0.71	0.43	0.020
38	--	6.2	6.7	--	0.42	0.74	0.44	0.024
39	--	6.5	7.0	--	0.34	0.75	0.46	0.029

[j] See Chart 4, p. 78, for possible structures.

[k] Measures C_{16} fragments in C_{22} and C_{32} coupling products of Chart 7, p. 198.

[l] mM, per mM perester taken; see heading O, p. 282. [m] See p. 247 for estimation procedure.

[n] Values at 11, 50, and 89% averaged with weights of 5/18, 4/9, and 5/18 (94).

Table 18 Selected Data for Least-Squares Calculations 1, 2, 3, 5, 11, 12, 13, 15, 16, and 17.[a]

	Calculation No. 1				Calculation No. 2			
RUN	$R1^{calc}$[b]	RELDEV[c] R1	$R2^{calc}$[d]	RELDEV[c] R2	$R1^{calc}$[b]	RELDEV[c] R1	$R2^{calc}$[d]	RELDEV[c] R2
1	1.38	-12.2	0.792	10.8	1.34	-14.4	0.810	13.2
2	2.45	- 8.5	0.513	5.2	2.48	- 7.5	0.512	5.1
3	3.65	3.9	0.383	- 2.3	3.77	7.2	0.378	- 3.7
4	4.92	9.6	0.307	- 8.4	5.15	14.7	0.300	-10.4
5	1.17	-13.3	0.820	6.6	1.12	-17.1	0.837	8.8
6	2.08	- 8.7	0.528	1.9	2.05	-10.1	0.528	1.9
7	3.09	6.1	0.394	- 1.5	3.10	6.5	0.389	- 2.7
8	4.16	2.1	0.315	- 2.9	4.23	3.7	0.309	- 4.8
9	1.03	6.3	0.839	9.9	1.01	3.7	0.822	7.8
10	1.82	12.4	0.541	0.2	1.80	11.0	0.527	- 2.3
11	2.70	8.7	0.404	- 0.3	2.69	8.5	0.392	- 3.3
12	3.63	28.6	0.324	- 7.2	3.65	29.3	0.313	-10.3
13	0.33	-27.6	0.032	- 3.4	0.33	-26.2	0.034	3.7
14	0.65	-13.9	0.020	- 2.5	0.66	-12.5	0.020	2.2
15	1.41	-14.1	0.012	- 6.0	1.43	-12.6	0.012	- 4.3
16	1.41	- 0.8	0.012	- 6.0	1.43	1.0	0.012	- 4.3
17	2.82	- 3.5	0.009	-12.8	2.88	- 1.5	0.009	-12.7
18	0.31	-14.5	0.051	- 1.0	0.31	-13.2	0.055	5.5
19	0.60	- 8.9	0.030	8.1	0.61	- 8.2	0.032	13.4
20	1.30	- 2.4	0.018	3.9	1.31	- 1.9	0.018	6.0
21	2.58	0.1	0.012	5.3	2.60	0.7	0.012	5.3
22	0.30	- 9.0	0.061	19.0	0.31	- 6.9	0.064	25.7
23	0.58	0.2	0.036	4.7	0.59	1.1	0.037	9.3
24	1.25	0.6	0.020	2.3	1.25	0.9	0.021	4.2
25	2.48	6.0	0.013	1.0	2.49	6.2	0.013	0.8
26	2.48	6.4	0.013	--	2.49	6.6	0.013	--
27	1.01	-11.2	1.248	6.6	0.93	-18.8	1.274	8.9
28	1.05	- 3.9	0.622	- 2.9	1.03	- 5.7	0.639	- 0.2
29	1.05	(-13.1)	0.342	- 2.4	1.07	(-11.7)	0.353	0.8
30	1.05	(- 5.3)	0.149	- 9.8	1.09	(- 1.4)	0.154	- 6.7
31	0.32	-14.8	0.037	(-15.6)	0.33	-13.5	0.040	(- 9.3)
32	0.42	(- 2.7)	0.013	(-37.3)	0.42	(- 1.6)	0.013	(-33.8)
33	0.42	(- 2.7)	0.013	(-40.3)	0.42	(- 1.6)	0.013	(-37.0)
34	0.43	(- 2.8)	0.007	(-39.9)	0.43	(- 1.8)	0.007	(-37.5)
35	0.43	(-14.3)	0.005	(-52.7)	0.43	(-13.5)	0.005	(-51.7)
36	3.26	(-20.4)	0.0042	4.3	3.33	(-18.7)	0.0042	4.3
37	3.12	(-10.9)	0.0039	8.4	3.16	(- 9.7)	0.0039	8.1
38	3.00	(- 9.2)	0.0037	- 3.5	3.02	(- 8.6)	0.0036	- 4.2
39	2.85	--	0.0034	- 7.0	2.85	--	0.0034	- 8.0

[a] See Table 19 for values of parameters and quality-of-fit quantities.

[b] % yield 5/% yield 10.

[c] (calc−obs) /obs x 100%; parentheses indicate points omitted from the least-squares optimization; see footnotes e and h, Table 17.

[d] % yield 6/% yield 5.

Table 18 (cont.)

	Calculation No. 3		Calculation No. 5				Calculation No. 11	
RUN	$R2^{calc\,d}$	$RELDEV^c$ R2	$R1^{calc\,b}$	$RELDEV^c$ R1	$R2^{calc\,d}$	$RELDEV^c$ R2	$R1^{calc\,b}$	$RELDEV^c$ R1
1	0.738	3.2	1.35	-13.90	0.762	6.63	1.42	- 9.9
2	0.509	4.6	2.48	- 7.40	0.511	4.94	2.52	- 6.0
3	0.400	2.1	3.76	7.07	0.395	0.75	3.75	6.8
4	0.327	- 2.3	5.14	14.50	0.320	- 4.52	5.08	13.1
5	0.776	0.9	1.12	-17.32	0.798	3.71	1.16	-14.4
6	0.530	2.3	2.04	-10.47	0.529	2.11	2.04	-10.5
7	0.413	3.3	3.08	5.90	0.406	1.52	3.02	3.8
8	0.337	3.7	4.21	3.21	0.328	0.83	4.08	- 0.1
9	0.805	5.5	0.98	1.10	0.806	5.63	1.00	3.4
10	0.547	1.3	1.77	8.96	0.536	- 0.77	1.74	7.5
11	0.425	5.0	2.65	6.82	0.411	1.43	2.56	3.2
12	0.346	- 0.7	3.60	27.72	0.332	- 4.86	3.43	21.7
13	0.029	-11.8	0.33	-26.19	0.031	- 5.10	0.38	-16.6
14	0.018	- 7.9	0.66	-12.32	0.019	- 4.08	0.71	- 5.7
15	0.012	- 6.5	1.44	-12.38	0.012	- 6.06	1.45	-11.7
16	0.012	- 6.5	1.44	1.20	0.012	- 6.06	1.45	2.0
17	0.009	-10.1	2.88	- 1.35	0.009	-11.30	2.77	- 5.4
18	0.047	- 8.9	0.31	-13.86	0.051	- 2.35	0.35	- 3.7
19	0.029	2.8	0.60	- 8.48	0.030	7.09	0.65	- 2.2
20	0.018	4.4	1.30	- 1.95	0.018	4.77	1.31	- 1.7
21	0.012	10.7	2.60	0.65	0.012	8.45	2.47	- 4.1
22	0.056	10.1	0.30	- 8.35	0.060	17.25	0.34	2.0
23	0.034	- 0.1	0.58	0.32	0.035	3.73	0.62	6.9
24	0.021	3.1	1.25	0.55	0.021	3.25	1.25	0.6
25	0.014	6.6	2.48	6.03	0.014	4.09	2.36	0.8
26	0.014	--	2.48	6.49	0.014	--	2.36	1.2
27	1.169	- 0.1	0.92	-19.15	1.21	3.37	0.96	-16.1
28	0.581	- 9.2	1.03	- 5.66	0.602	- 5.96	1.08	- 1.1
29	0.319	- 8.8	1.07	-11.47	0.331	- 5.47	1.13	(- 6.6)
30	0.139	-15.9	1.10	- 0.99	0.144	-12.92	1.17	(4.9)
31	0.034	(-22.7)	0.33	-13.62	0.037	(-16.79)	0.37	- 2.8
32	0.012	(-41.3)	0.42	- 1.42	0.012	(-38.14)	0.47	(9.1)
33	0.012	(-44.1)	0.42	- 1.42	0.012	(-41.09)	0.47	(9.1)
34	0.007	(-42.8)	0.43	- 1.57	0.007	(-40.61)	0.48	(8.8)
35	0.005	(-54.4)	0.43	-13.21	0.005	(-53.32)	0.48	(- 4.1)
36	0.0041	3.0	3.34	-18.54	0.0041	2.86	3.18	(-22.5)
37	0.0039	7.8	3.17	- 9.51	0.0039	7.74	3.01	(-14.1)
38	0.0037	- 3.5	3.02	- 8.41	0.0037	- 3.43	2.86	(-13.4)
39	0.0035	- 6.1	2.85	--	0.0035	- 6.07	2.69	--

Table 18 (cont.)

	Calculation No. 12				Calculation No. 13			
					R^{f}			
RUN	$R1^{calc^{b}}$	RELDEV^{c} R1	$R2^{calc^{d}}$	RELDEV^{c} R2	OBSVD	CALC	$R2^{calc^{d}}$	RELDEV^{c} R2
1	1.55	- 1.2	0.691	- 3.3	1.87	1.89	0.729	2.0
2	2.64	- 1.6	0.491	0.9	1.98	2.00	0.502	3.0
3	3.63	3.4	0.408	4.1	2.27	2.17	0.402	2.5
4	4.43	- 1.4	0.361	7.8	2.40	2.41	0.341	1.8
5	1.23	- 8.7	0.741	- 3.7	2.09	2.28	0.772	0.4
6	2.13	- 6.8	0.514	- 0.9	2.23	2.39	0.521	0.7
7	2.98	2.4	0.417	4.2	2.62	2.55	0.411	2.7
8	3.73	- 8.5	0.360	10.8	2.54	2.75	0.343	5.5
9	1.03	6.0	0.781	2.4	2.79	2.63	0.805	5.5
10	1.78	9.8	0.534	- 1.1	3.01	2.74	0.539	- 0.3
11	2.52	1.8	0.427	5.4	3.95	2.89	0.420	3.6
12	3.21	13.7	0.363	4.1	3.52	3.08	0.347	- 0.5
13	0.37	-18.5	0.029	-12.3	2.02	2.47	0.030	- 8.6
14	0.72	- 4.7	0.018	- 9.9	2.43	2.55	0.019	- 7.1
15	1.50	- 8.8	0.012	- 9.0	2.48	2.72	0.012	- 8.0
16	1.50	5.3	0.012	- 9.0	2.87	2.72	0.012	- 8.0
17	2.73	- 6.5	0.009	- 9.9	2.84	3.03	0.009	-11.4
18	0.33	- 7.7	0.048	- 8.1	2.53	2.73	0.049	- 4.9
19	0.64	- 2.9	0.029	1.8	2.74	2.82	0.029	4.4
20	1.33	0.2	0.017	2.4	3.01	2.99	0.018	3.0
21	2.45	- 5.2	0.012	11.6	3.14	3.31	0.012	8.9
22	0.32	- 3.3	0.057	11.7	2.75	2.83	0.059	15.2
23	0.61	5.2	0.034	- 0.6	3.08	2.92	0.035	1.7
24	1.27	2.1	0.020	1.3	3.17	3.10	0.020	1.8
25	2.33	- 0.3	0.014	7.5	3.40	3.41	0.014	4.7
26	2.33	0.1	0.014	--	3.42	3.41	0.014	--
27	1.02	-10.4	1.120	- 4.3	2.12	2.37	1.172	0.1
28	1.15	5.4	0.554	-13.5	2.31	2.19	0.580	- 9.4
29	1.20	(- 0.7)	0.303	-13.4	2.09	2.10	0.318	- 9.1
30	1.24	(11.4)	0.131	-20.4	2.28	2.04	0.138	-16.5
31	0.36	- 5.4	0.034	(-22.7)	2.43	2.56	0.035	(-19.6)
32	0.46	(7.7)	0.012	(-41.7)	2.79	2.58	0.012	(-39.9)
33	0.46	(7.7)	0.012	(-44.5)	2.79	2.58	0.012	(-42.8)
34	0.47	(7.6)	0.007	(-43.2)	2.79	2.59	0.007	(-41.9)
35	0.47	(- 5.1)	0.005	(-54.7)	2.46	2.59	0.005	(-54.0)
36	3.07	(-25.2)	0.0041	2.1	2.35	3.14	0.0041	2.2
37	2.92	(-16.7)	0.0039	7.6	2.70	3.23	0.0039	7.7
38	2.78	(-15.7)	0.0037	- 2.9	2.83	3.35	0.0037	- 2.9
39	2.62	--	0.0035	- 4.7	--	3.51	0.0035	- 4.9

[f] % yield **10** x (⌬)$_{av}$/% yield **5**.

Table 18 (cont.)

	Calculation No. 15				Calculation No. 16		Calculation No. 17	
RUN	$R1^{calc^b}$	$RELDEV^c$ R1	$R2^{calc^d}$	$RELDEV^c$ R2	$R2^{calc^d}$	$RELDEV^c$ R2	$R2^{calc^d}$	$RELDEV^c$ R2
1	1.56	-0.5	0.742	3.8	0.756	5.8	0.754	5.5
2	2.68	0.0	0.507	4.1	0.513	5.3	0.503	3.2
3	3.71	5.7	0.404	3.2	0.401	2.2	0.386	-1.4
4	4.55	1.3	0.342	2.2	0.328	-2.1	0.311	-7.1
5	1.24	-8.5	0.771	0.3	0.786	2.3	0.814	5.8
6	2.15	-5.8	0.516	-0.3	0.522	0.8	0.542	4.5
7	3.03	4.0	0.405	1.2	0.402	0.5	0.416	4.0
8	3.80	-6.8	0.337	3.7	0.325	0.1	0.335	3.2
9	1.02	5.0	0.800	4.8	0.807	5.8	0.789	3.4
10	1.78	9.7	0.529	-2.1	0.534	-1.2	0.539	-0.2
11	2.54	2.2	0.409	1.0	0.408	0.8	0.419	3.4
12	3.23	14.7	0.337	-3.5	0.330	-5.5	0.341	-2.2
13	0.37	-17.8	0.032	-3.4	0.032	-3.0	0.031	-5.0
14	0.72	-4.1	0.020	-0.3	0.020	-0.3	0.018	-12.3
15	1.50	-8.4	0.013	-0.6	0.013	0.1	0.010	-26.3
16	1.50	5.8	0.013	-0.6	0.013	0.1	0.010	-26.3
17	2.74	-6.0	0.010	-4.4	0.010	-3.0	0.006	-42.3
18	0.34	-6.5	0.049	-5.3	0.051	-2.0	0.054	4.4
19	0.65	-1.8	0.029	4.6	0.030	7.1	0.031	10.9
20	1.34	1.1	0.028	3.9	0.018	4.5	0.017	0.7
21	2.46	-4.5	0.012	10.5	0.012	8.1	0.010	-6.1
22	0.32	-2.2	0.058	13.4	0.060	17.9	0.064	25.2
23	0.62	6.4	0.034	0.3	0.035	3.5	0.037	9.4
24	1.28	3.0	0.020	0.7	0.020	2.2	0.021	3.5
25	2.35	0.4	0.014	4.1	0.013	2.4	0.013	-3.7
26	2.35	0.8	0.014	--	0.013	--	0.013	--
27	1.01	-11.4	1.174	0.3	1.193	2.0	1.219	4.2
28	1.16	6.6	0.579	-9.5	0.594	-7.1	0.618	-3.5
29	1.23	(1.5)	0.317	-9.4	0.329	-5.9	0.340	-2.8
30	1.28	(14.9)	0.137	-17.0	0.147	-10.9	0.145	-12.1
31	0.36	-4.4	0.036	(-17.2)	0.037	(-15.9)	0.038	(-13.9)
32	0.47	(8.2)	0.013	(-34.7)	0.013	(-35.7)	0.010	(-48.9)
33	0.47	(8.2)	0.013	(-37.8)	0.013	(-38.8)	0.010	(-51.3)
34	0.47	(7.0)	0.008	(-35.5)	0.008	(-36.3)	0.004	(-65.4)
35	0.47	(-6.5)	0.006	(-49.8)	0.006	(-48.4)	0.002	(-83.3)
36	3.07	(-25.2)	0.0040	-0.8	0.0050	(25.8)	0.0003	(-92.1)
37	2.91	(-16.8)	0.0038	6.1	0.0044	(22.0)	0.0004	(-88.8)
38	2.78	(-15.9)	0.0036	-2.9	0.0038	(1.0)	0.0005	(-86.2)
39	2.61	--	0.0035	-3.7	0.0033	(-10.3)	0.0007	(-80.6)

Table 19. Quality-of-fit Quantities and Values of Parameters for Least-Squares Calculations 1—20

Quantity[a]	Calculation No.				
	1	2	3	4	5
RUSD[b]	0.0860	0.0945	0.0868	0.0877	0.0846
AVDEV, %[c]	6.07	6.82	5.94	6.04	5.76
AVDEV R1	8.27	8.96	8.33	8.31	8.58
AVDEV $R1_1$	6.59	6.08	6.69	6.69	6.05
AVDEV $R1_2$	9.65	11.30	9.68	9.64	10.65
AVDEV R2	4.91	5.72	4.67	4.85	4.29
AVDEV $R2_1$	5.66	6.46	5.95	6.26	5.66
AVDEV $R2_2$	4.72	5.55	4.35	4.50	3.97
γ[f]	0.60	0.60	0.60	0.60	0.60
δ[f]	0.42	0.42	0.42	0.42	0.42
ϵ[g]	--	--	--	--	--
C	0.00	1.00	0.00	0.00	1.00
$\phi(20^\circ)$[d]	1.00	1.00	1.60	1.60	1.60
$E(100^\circ)$	0.138	0.142	0.139	0.139	0.142
E(Eact)	- 0.62	- 0.77	- 0.62	- 0.62	- 0.78
$F(100^\circ)$	0.0751	0.0564	0.0614	0.0624	0.0605
F(Eact)	(0.00)[a]	(0.00)[a]	(0.00)[a]	(0.00)[a]	(0.00)[a]
$G(100^\circ)$	1.530	1.313	1.247	1.211	1.176
G(Eact)	-13.21	-13.32	-13.07	-13.17	-13.26
$H(100^\circ)$[e]	18.6	3.9	23.9	33.3	5.6
$I(100^\circ)$	0.0039	0.0038	0.0038	0.0038	0.0038
I(Eact)	- 2.13	- 2.09	- 2.02	- 2.09	- 1.97

Table 19 (cont.)

Quantity[a]	Calculation No. 6	7	8	9	10
RUSD[b]	0.0872	0.0846	0.0866	0.0863	0.0856
AVDEV, %[c]	6.04	5.78	5.78	5.76	5.76
AVDEV R1	8.76	8.43	8.40	8.84	8.63
AVDEV $R1_1$	6.08	6.29	6.01	5.88	5.84
AVDEV $R1_2$	10.94	10.19	10.34	11.27	10.92
AVDEV R2	4.62	4.38	4.42	4.16	4.27
AVDEV $R2_1$	5.83	5.84	5.50	5.82	5.64
AVDEV $R2_2$	4.34	4.03	4.16	3.78	3.95
γ[f]	0.60	0.60	0.60	0.60	0.60
δ[f]	0.42	0.42	0.42	0.42	0.42
ϵ[g]	--	--	--	--	--
C	1.00	0.50	1.00	1.50	1.50
$\phi(20^\circ)$[d]	1.30	1.60	2.00	1.60	2.00
E(100°)	0.142	0.140	0.142	0.143	0.143
E(Eact)	- 0.78	- 0.70	- 0.79	- 0.84	- 0.85
F(100°)	0.0592	0.0609	0.0626	0.0596	0.0622
F(Eact)	(0.00)[a]	(0.00)[a]	(0.00)[a]	(0.00)[a]	(0.00)[a]
G(100°)	1.240	1.205	1.116	1.159	1.103
G(Eact)	-13.27	-13.17	-13.25	-13.30	-13.29
H(100°)[e]	4.6	8.6	7.3	3.7	4.3
I(100°)	0.0038	0.0038	0.0038	0.0038	0.0037
I(Eact)	- 2.08	- 2.06	- 1.75	- 2.00	- 1.76

Table 19 (cont.)

Quantity[a]	Calculation No.				
	11	12	13	14	15
RUSD[b]	0.0722	0.0827	0.0670	0.0858	0.0650
AVDEV, %[c]	5.03	5.89	4.57	5.75	4.37
AVDEV R1	6.47	5.12	5.13	8.69	5.13
AVDEV $R1_1$	4.12	4.35	4.30	6.31	4.30
AVDEV $R1_2$	8.38	5.74	5.79	10.63	5.80
AVDEV R2	4.28	6.29	4.28	4.21	3.99
AVDEV $R2_1$	5.41	5.84	5.54	4.41	3.51
AVDEV $R2_2$	4.01	6.40	3.98	4.16	4.10
γ[f]	0.00	0.60	0.60	0.60	0.60
δ[f]	0.45	0.42	0.42	0.42	0.39
ϵ[g]	0.40	--	--	0.28	--
C	1.00	1.00	1.00	1.00	1.00
$\phi(20°)$[d]	1.60	1.60	1.60	1.60	1.60
E(100°)	0.136	0.154	0.154	0.144	0.154
E(Eact)	- 0.92	- 1.00	- 1.01	- 0.77	- 1.05
F(100°)	0.0643	0.0665	0.0680	0.0657	0.0846
F(Eact)	(0.00)[a]	(0.00)[a]	(0.00)[a]	(0.00)[a]	(0.00)[a]
G(100°)	1.149	1.166	1.243	1.180	1.362
G(Eact)	-13.41	-13.31	-13.42	-13.36	-13.60
H(100°)	6.4	19.9	14.3	11.9	to high to measure
I(100°)	0.0038	0.0038	0.0038	0.0035	0.0035
I(Eact)	- 1.89	- 1.86	- 1.82	- 1.84	- 1.58

Table 19 (cont.)

Quantity[a]	Calculation No.				
	16	17	18	19	20
RUSD[b]	0.0831	0.1032	0.0857	0.0847	0.0859
AVDEV, %[c]	5.32	6.68	5.90	5.79	5.81
AVDEV R1	8.46	9.28	8.52	8.49	8.78
AVDEV $R1_1$	6.02	6.44	6.04	6.23	5.88
AVDEV $R1_2$	10.48	11.63	10.53	10.33	11.15
AVDEV R2	3.53	5.20	4.52	4.38	4.26
AVDEV $R2_1$	3.62	13.97	5.46	5.93	5.69
AVDEV $R2_2$	3.52	4.10	4.29	4.01	3.91
γ[f]	0.60	0.60	0.60	0.60	0.60
δ[f]	0.42	0.42	0.42	0.42	0.42
ϵ[g]	--	--	--	--	--
C	1.00	1.00	1.00	1.00	1.00
ϕ(20°)	1.60	1.60	1.60	1.60	1.60
E(100°)	0.142	0.138	0.144	0.141	0.143
E(Eact)	- 0.79	- 0.82	- 0.78	- 0.75	- 0.83
F(100°)	0.0642	0.0608	0.0606	0.0631	0.0591
F(Eact)	(0.00)[a]	(0.00)[a]	(0.00)[a]	(1.00)[a]	(-1.00)[a]
G(100°)	1.189	1.329	1.152	1.197	1.175
G(Eact)	-13.18	-13.02	-13.32	-12.78	-13.71
H(100°)[e]	8.5	2.0	(10^{10})	5.5	5.2
I(100°)	0.0046	(0.)[a]	0.0038	0.0038	0.0038
I(Eact)	- 4.10	--	- 1.94	- 1.97	- 2.06

Footnotes for Table 19

[a] Values of parameters are shown between the second and third solid horizontal lines. Those above the dotted line and those below the dotted line but encased in parentheses are assumed values; all others shown were determined in the least-squares optimization. Product ratio and other data for some of these calculations may be found in Tables 17 and 18.

[b] Defined by eq. 2.4-1, p. 246. Values quoted are felt to be good to ± one or two units in the last place.

[c] Eq. 2.4-3, p. 248. In AVDEV RI_J quantities, R1 ≡ % yield 5/% yield 10, R2 ≡ % yield 6/% yield 5, and J gives the identity of the starting perester (ring-opened perester 1 or ring-closed perester 2).

[d] Equation of form of eq. 2.4-14 employed, where preexponential factor is unity and composite activation energy is chosen to give $\phi(20°)$ as listed. Exception is Calculation 4, where we have taken $\phi = 1.6$ at all temperatures.

[e] Composite activation energy of -8 kcal/mole assumed for the parameter H; see heading K, p. 277.

[f] Values of these parameters in all cases are such that, with E chosen to optimize the product ratios, the calculated yields of ring-opened hydrocarbon 5 average no more than 3% greater or less than the observed yields. See Chart 7, p. 198 for definitions of γ and δ.

[g] Fit to product ratios R1 and R2 independent of this quantity. Values shown were chosen to give yields of tetrahydronaphthalenes 8 correctly; see Table 17, footnote j. See Chart 7, p. 198, for meaning of ϵ.

APPENDIX B. Kinetic Treatment of Perester Decomposition in the Presence of 1, 4-Cyclohexadiene

We derive here kinetic expressions for decomposition of the ring-opened and ring-closed peresters **1** and **2** in the presence of 1, 4-cyclohexadiene based on processes depicted in Chart 7, p. 198.

Chart 7 shows that we are concerned with the concentrations of six free-radical intermediates. Starting from perester **1** and invoking the steady-state approximation for each reactive intermediate, we obtain six equations (ZH ≡ 1, 4-cyclohexadiene; Z· ≡ cyclohexadienyl radical; P ≡ perester):

$$d(\cdot\mathrm{O}\underline{t}\mathrm{Bu})/dt = (\alpha+\omega)k_o(\mathrm{P}) - k_{fast}(\cdot\mathrm{O}\underline{t}\mathrm{Bu})(\mathrm{ZH}) = 0 \qquad \text{(B 1)}$$

$$d(\underset{\sim\sim}{22})/dt = \omega k_o(\mathrm{P}) - k_5(\underset{\sim\sim}{22})(\mathrm{ZH}) - k_6(\underset{\sim\sim}{22})(\mathrm{Z}\cdot) = 0 \qquad \text{(B2)}$$

$$\begin{aligned} d(\underset{\sim}{3})/dt = \alpha k_o(\mathrm{P}) - \left\{k_1 + k_r + k_a^{\bigcirc}(\mathrm{ZH}) + k_a^{\odot}(\mathrm{Z}\cdot)\right\}(3) \\ + k_2(\underset{\sim}{4}) + k_{-r}(\underset{\sim}{9}) = 0 \qquad \text{(B3)} \end{aligned}$$

$$d(\underset{\sim}{4})/dt = k_1(\underset{\sim}{3}) - \left\{k_2 + k_b^{\bigcirc}(\mathrm{ZH}) + k_b^{\odot}(\mathrm{Z}\cdot) + k_7(\underset{\sim}{9})\right\}(\underset{\sim}{4}) = 0 \qquad \text{(B4)}$$

$$d(\underset{\sim}{9})/dt = k_r(\underset{\sim}{3}) - \left\{k_{-r} + 2k_3(\underset{\sim}{9}) + k_d(\mathrm{Z}\cdot) + k_7(\underset{\sim}{4})\right\}(\underset{\sim}{9}) = 0 \qquad \text{(B5)}$$

$$\begin{aligned} d(\mathrm{Z}\cdot)/dt = k_{fast}(\cdot\mathrm{O}\underline{t}\mathrm{Bu})(\mathrm{ZH}) + \left\{k_5(\underset{\sim\sim}{22}) + k_a^{\bigcirc}(\underset{\sim}{3}) + k_b^{\bigcirc}(\underset{\sim}{4})\right\}(\mathrm{ZH}) \\ - \left\{k_6(\underset{\sim\sim}{22}) + k_a^{\odot}(\underset{\sim}{3}) + k_b^{\odot}(\underset{\sim}{4}) + k_d(\underset{\sim}{9}) + 2k_4(\mathrm{Z}\cdot)\right\}(\mathrm{Z}\cdot) = 0 \qquad \text{(B6)} \end{aligned}$$

The concentrations of ·O$\underline{t}$Bu and the lactonyl radical **22** can be eliminated from eq. 6 using eqs. 1 and 2:

$$d(Z\cdot)/dt = \alpha k_o(P)\ \left\{1 + 2A\left[\frac{B(ZH)/(Z\cdot)}{1+B(ZH)/(Z\cdot)}\right]\right\} + \left\{k_a^{\obar}(3) + k_b^{\obar}(4)\right\}(ZH)$$

$$- \left\{k_a^{\odot}(3) + k_b^{\odot}(4) + k_d(9) + 2k_4(Z\cdot)\right\}(Z\cdot) = 0 \qquad \text{(B7)}$$

We have employed in eq. 7 the definitions of the parameters A and B given in eqs. 2. 1-4.

We now have, in eqs. 3, 4, 5, and 7, four equations in four unknowns. To eliminate one of the unknowns we add eqs. 3 and 4 to get

$$\alpha k_o(P) + k_{-r}(9) = \left\{k_r + k_a^{\obar}(ZH) + k_a^{\odot}(Z\cdot)\right\}(3)$$

$$+ \left\{k_b^{\obar}(ZH) + k_b^{\odot}(Z\cdot) + k_7(9)\right\}(4) \quad , \qquad \text{(B8)}$$

and make the assumption that interconversion of 3 and 4 is much faster than any other processes the two take part in; specifically, we assume $(4) = k_1(3)/k_2$. Eq. 8 thus becomes after substitution and rearrangement:

$$W \equiv k_r(3)/\alpha k_o(P) =$$

$$\frac{1 + k_{-r}(9)/\{\alpha k_o(P)\}}{1 + E(1+I)(ZH) + \left(\dfrac{k_b^{\odot}k_r}{k_2 k_r}\right)(1 + 1/H)(Z\cdot) + \left(\dfrac{k_1 k_7}{k_2 k_r}\right)(9)} \qquad \text{(B9)}$$

Eq. 9 is destined to become eq. 2. 1-9.

We can now write the concentrations of 3 and 4 which appear in eqs. 5 and 7 in terms of the newly defined variable W. Eq. 5 is simply quadratic in (9), and as such we can solve explicitly for (9). The usual form for the roots of the quadratic equation $ax^2 + bx + c = 0$ is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad .$$

As we have in eq. 5 a, b > 0 but c < 0, we must take the upper sign. For reasons which once appeared compelling, we have used the equivalent relationship (for the upper sign)

$$x = \frac{-2c}{b + \sqrt{b^2 - 4ac}} \quad .$$

We find (using eq. 13 below for the second step)

$$\underset{\sim}{(9)} = \frac{2\alpha k_o(P)W}{k_d(Z\cdot)\,S(1+T)} = \frac{2W}{S(1+T)}\left(2\alpha k_o(P)X/k_3\right)^{\frac{1}{2}} \tag{B10}$$

where the shorthand expressions S and T (eqs. 2.1-5 and 2.1-6) are given the definitions

$$S \equiv 1 + \left(\frac{k_7 k_1}{k_2 k_r}\right)\left(\frac{\alpha k_o(P)W}{k_d(Z\cdot)}\right) + \frac{k_{-r}}{k_d(Z\cdot)} \quad ; \tag{B11}$$

$$T \equiv \left\{1 + \frac{8\alpha k_o(P)k_3 W}{\left[k_d(Z\cdot)\right]^2 S^2}\right\}^{\frac{1}{2}} \quad . \tag{B12}$$

If we now substitute for $\underset{\sim}{(9)}$ in eqs. 9 and 7, make use of the definition

$$X \equiv \frac{\alpha k_o(P)k_3}{2k_d^{\,2}(Z\cdot)^2} \tag{B13}$$

to replace (Z·), and invoke the definitions of the parameters C, D, F and G given in eqs. 2.1-4, we find that eq. 9 becomes eq. 2.1-9, eq. 7 becomes 2.1-10, and the expressions for S and T become eqs. 2.1-5 and 2.1-6, respectively.

Had we started with ring-closed perester 2 instead of ring-opened perester 1, the initial set of six steady-state equations would have differed in form from those given here only in that the term $\alpha k_o(P)$ would have appeared in eq. 4 instead of eq. 3. As we employed only the sum of eqs. 3 and 4 in this derivation, this distinction is inconsequential, provided that we again assume that 3 and 4 are in rapid equilibrium. Thus, in all of the final equations we can simply take (P) to be the concentration of the perester employed, whether it be 1 or 2, and k_o to be the rate constant for thermal decomposition of that perester. Of course $A = 0$ for perester 2 (p. 204).

We obtain for the product yields eqs. 2.1-1—2.1-3 as follows. We first write

$$d(5)/dt = \left\{k_a^{\bigcirc}(ZH) + k_a^{\circledcirc}(Z\cdot)\right\}(3) \quad , \qquad \text{(B14)}$$

so that

final concentration of hydrocarbon 5 =

$$= \alpha \int_0^\infty \left\{k_a^{\bigcirc}(ZH) + k_a^{\circledcirc}\left(\frac{\alpha k_o(P)k_3}{2k_d{}^2X}\right)^{\frac{1}{2}}\right\}\left(\frac{k_o(P)W}{k_r}\right)dt$$

$$= \alpha \int_0^\infty \left\{E(ZH) + (G/H)\left(\frac{\alpha k_o(P)}{2X}\right)^{\frac{1}{2}}\right\} k_o(P)dt$$

where we have substituted for $(\underset{\sim}{3})$ and for (Z·) using eqs. 9 and 13 and then for other groupings of rate constants using eqs. 2.1-4.

We now pass from an integral over time to an integral over the perester concentration using the relationship

$$-\,d(P)/dt = k_o(P) \quad ,$$

or

$$dt = -\,d(P)/k_o(P) \quad .$$

When t = 0, (P) = $(P)_o$; when t = ∞, (P) = 0. Therefore we can write

$$\text{final conc } \underset{\sim}{5} = \alpha \int_0^{(P)_o} \left\{ E(ZH) + (G/H)\left(\frac{\alpha k_o(P)}{2X}\right)^{\frac{1}{2}} \right\} d(P) \quad . \qquad \text{(B15)}$$

We now introduct the integration variable $z \equiv (P)/(P)_o$ into eq. 15. The result is:

$$\text{final conc } \underset{\sim}{5} = \alpha(P)_o \int_0^{1} \left\{ E(ZH) + (G/H)\left(\frac{\alpha k_o(P)_o z}{2X}\right)^{\frac{1}{2}} \right\} dz$$

which gives eq. 2.1-1 since % yield $\underset{\sim}{5}$ = 100(final conc $\underset{\sim}{5}$)/$(P)_o$.

Eqs. 2.1-2 and 2.1-3 are obtained in the same way starting from

$$d(\underset{\sim}{6})/dt = \left\{ k_b^{\bigcirc}(ZH) + k_b^{\odot}(Z\cdot) + k_7(\underset{\sim}{9}) \right\} (\underset{\sim}{4}) \qquad \text{(B16)}$$

and

$$d(\underset{\sim}{10})/dt = \left\{ (\tfrac{1}{2}\gamma)\, 2k_3(\underset{\sim}{9}) + \delta k_d(Z\cdot) + k_7(\underset{\sim}{4}) \right\} (\underset{\sim}{9}) \quad . \qquad \text{(B17)}$$

Finally, we need expressions for the precent yield of tetrahydronaphthalenes B and for C_{16} groups which become incorporated in dimer via pairwise combination of ring-cyclized radicals or combination of a ring-cyclized radical with a cyclohexadienyl radical. The equations are

$$d(B)/dt = \left\{(\tfrac{1}{2}\gamma)\,2k_3(9) + \epsilon k_d(Z\cdot)\right\}\,(9)$$

and

$$d(C_{16} \text{ groups in dimer})/dt = \left\{(1-\gamma)\,2k_3(9) + (1-\delta-\epsilon)k_d(Z\cdot)\right\}\,(9)$$

which give by comparison to eq. 17 easily deduced modifications of eq. 2.1-3.

The range of integration of zero to one in the equations for the product yields permits direct application of the well-known formulas for Gaussian quadrature (94). We note that the integrands of eqs. 2.1-1 and 2.1-3 are insensitive to the value of the integration variable z (i.e., to the instantaneous perester concentration) for values of the arabic-letter parameters which fit the product-ratio data and that the integrand of eq. 2.2-2 for % yield 6 goes only approximately as the square root of z or of (P). This moderate behavior allows us to employ the three-point quadrature formula with insignificant loss of accuracy. This entails evaluating the various integrands for $z = 0.1127\ldots$, $0.500\ldots$, and $0.88729\ldots$ (i.e., for approximately 11, 50, and 89% reaction). These values are then summed using weighting factors of 5/18, 4/9, and 5/18, respectively.

There is but one remaining consideration, that concerning how we take into account the diminution of the 1,4-cyclohexadiene concentration, incurred in its capacity as hydrogen donor, as the reaction proceeds. The quadrature formalism requires instantaneous cyclohexadiene concentrations at 11, 50 and 89% reaction. The prior consumption of 1,4-cyclohexadiene at these points can be estimated using the following equations, where subscripts designate values of the integration variable z for which various quantities are to be evaluated:

$$\begin{aligned}
(\mathrm{ZH})_{0.11} - (\mathrm{ZH})_{0.} &\cong 0.11\,(\mathrm{P})_o \Big(d(\mathrm{ZH})/d(\mathrm{P})\Big)_{0.11} \\
(\mathrm{ZH})_{0.50} - (\mathrm{ZH})_{0.11} &\cong \frac{0.39}{2}\,(\mathrm{P})_o \Big\{\Big(d(\mathrm{ZH})/d(\mathrm{P})\Big)_{0.50} \\
&\qquad + \Big(d(\mathrm{ZH})/d(\mathrm{P})\Big)_{0.89}\Big\} \\
(\mathrm{ZH})_{0.89} - (\mathrm{ZH})_{0.50} &\cong \frac{0.39}{2}\,(\mathrm{P})_o \Big\{\Big(d(\mathrm{ZH})/d(\mathrm{P})\Big)_{0.89} \\
&\qquad + \Big(d(\mathrm{ZH})/d(\mathrm{P})\Big)_{0.50}\Big\}
\end{aligned} \tag{B18}$$

The instantaneous concentrations of 1,4-cyclohexadiene are then obtained as the initial concentration less the sum of the first one, two, or three equations for 11, 50 and 89% reaction. The key feature of this approach is that the time-consuming extraction of the roots W and X of eqs. 2.1-9 and 2.1-10 need not be carried out for any values of z in addition to those employed in the basic quadrature formulas.

With reference to Chart 7 we can write

$$-\,d(\mathrm{ZH})/dt = \Big\{k_{fast}(\cdot\,\mathrm{O}\underline{t}\mathrm{Bu}) + k_5(\underset{\sim}{22}) + k_a^{\text{⌬}}(\underset{\sim}{3}) + k_b^{\text{⌬}}(\underset{\sim}{4})\Big\}\ (\mathrm{ZH})$$

from which we obtain, using eqs. 1, 2, 9, 12, and 2.1-4 in conjunction with $-d(P)/dt = k_o(P)$:

$$d(ZH)/d(P) = 0.8\alpha\left\{1 + \frac{2AB(ZH)\left(\frac{\alpha k_o(P)_o z}{2X}\right)^{\frac{1}{2}}}{1 + B(ZH)\left(\frac{\alpha k_o(P)_o z}{2X}\right)^{\frac{1}{2}}} + E(ZH)(1 + I)W\right\} \qquad (B19)$$

The factor of 0.8 in the above is meant to broadly account for regeneration of some of the 1,4-cyclohexadiene molecules which become cyclohexadienyl radicals upon reaction of the latter with themselves or other radicals. For example, conversion of a ring-cyclized radical to dihydronaphthalene 10 via reaction with cyclohexadienyl radical also produces either 1,4-cyclohexadiene or 1,3-cyclohexadiene. By analogy to gas phase results (52) we expect that twice as much 1,4-cyclohexadiene will be formed in this way as 1,3-cyclohexadiene.

Eq. 19 and eqs. 2.1-9 and 2.1-10 for the variables W and X show that the problem is technically more complex than we have indicated, because values of (ZH), W, and X at each of the three integration points are interdependent. Thus one might assume values of W and X for use in eq. 19, obtain the instantaneous values of (ZH) via eqs. 18, put these into eqs. 2.1-9 and 2.1-10, solve those equations for W and X, put the new values into eq. 19, and iterate to self-consistency. This is the approach taken, except that the iteration to self-consistency is accomplished not within a single least-squares iteration on the parameters, but over several such cycles. For the first cycle of a series, initial approximations to W and X were obtained from empirically derived relationships. The values so obtained were employed to estimate the instantaneous cyclohexadiene concentrations and then as initial approximations to W and X in the iterative extraction of the values of these variables which satisfy eqs. 2.1-9 and 2.1-10. The resultant values were used as the initial approximations to W and X in the next cycle. Provided that the series of iterations converges, this approach results in the availability of better and better approximations to W and X for use in eqs. 18 and 19. This eventually allows the instantaneous cyclohexadiene concentrations to be calculated correctly. In practice, 'eventually' works out to be three or four cycles.

SECTION THREE: NATURE OF THE RADICAL INTERMEDIATES

1. Approaches to the Definition of Nonclassical Character

Free radicals are characterized by the presence of an unpaired electron. In the methyl radical, the ethyl radical, and by analogy the _n_-dodecyl radical, the odd electron appears to be localized on a particular carbon. In the allyl radical and the triphenylmethyl radical, abundant information indicates that the odd electron is distributed over a number of carbon atoms. Neither of these types of radicals would be considered, by analogy with the use of the term in carbonium-ion chemistry, to be nonclassical.

What we have in mind in speaking of nonclassical character is essentially a species which has more than a single significant radical center but one in which the requisite delocalization arises other than through a π-electron system. Adapting Bartlett's definition from carbonium-ion chemistry, we may say that _a free radical is nonclassical if its ground state has delocalized bonding σ electrons (114)_.

This definition identifies the preeminent characteristic most people seem to intuitively take to distinguish the nonclassical radical from the types considered in the opening paragraph. But it is not an operational definition: it does not tell us how the presence or absence of σ-electron delocalization may be determined. In principle, an operational definition is not needed; one could simply carry out a series of quantum-mechanical calculations as a function of geometry, find the equilibrium configuration, and analyze the resultant wave function for the presence or absence of 'significant' σ-electron delocalization in the half-filled orbital. Although some presently available calculational schemes can be used in such an approach, judgements reached in this way have a sterile flavor because of the necessity for rather extensive approximations and because the results of such calculations are often not reliably translated into experimental predictions.

It is necessary therefore to make use of any of several derivative criteria. These may be broadly classed as structural, energetic, spectroscopic, kinetic, and mechanistic.

Let us imagine that a σ bond connects atoms A and B in a generalized molecule in which a carbon-hydrogen bond exists at center C. Further suppose that the above-mentioned hydrogen atom is dissociated with no change in geometry of the atomic arrangement. It may be, when this hypothetical state is allowed to relax, that molecular deformation will be restricted to angular changes about C, with C continuing to be the radical center. But it may also happen that the odd electron becomes strongly delocalized over centers A and B as well.* If this is so, it must be that three electrons--the odd electron plus the two which originally made up the A–B single bond--are asked to support two or perhaps three potentially strong interactions of bonding character between the centers A, B, and C. A probable result will be a diminished concentration of electrons in the region between centers A and B and

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*It may of course be that formation of a delocalized structure in an activated process.

a resultant increase in the equilibrium A–B distance with respect to that in the hydrocarbon. Similarly, we expect increased B–C and A–C distances with respect to the isomeric hydrocarbons having B–C and A–C bonds and carbon-hydrogen bonds at A and B. That is, σ-electron delocalization should have structural ramifications which are predictable in kind, if not always in degree.

The model chosen here serves to point out that there will be classical radical alternatives in situations wherein a nonclassical radical might form; the initially formed radical center at C might not have become delocalized, or rearrangement might have resulted in a bond between B and C with an essentially nondelocalized radical center at A or a bond between A and C with the B becoming the radical center. The possibilities are then that the configuration of minimum energy (a) corresponds to a σ-electron delocalized species or (b) has a geometry appropriate for one of the classical radical alternatives. In either case, stability alone need not determine from what species the products arise--the relative reactivities of the various possible species will also be important.

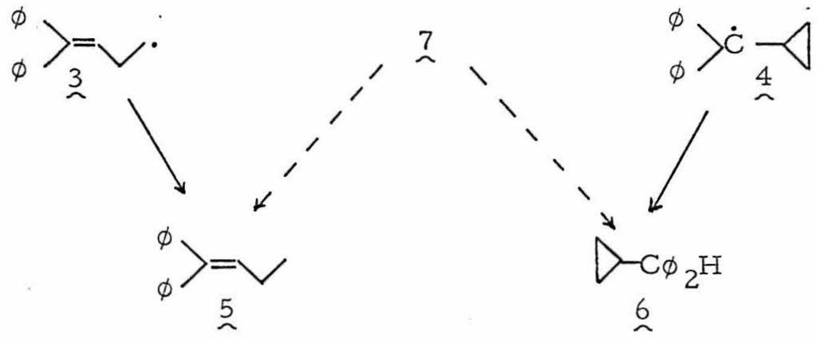
An unstable radical species can not, like a stable hydrocarbon, be subjected to structural analysis by X-ray or electron diffraction or be quantitatively combusted to obtain a heat of formation or a binding energy. To be sure, combination of the C–H bond dissociation energy in the above example with the heats of formation of the dissociated hydrogen atom and the starting hydrocarbon yields the heat of formation of the derived radical. But whether the latter quantity is 'unusual' would probably be judged on the basis of the C–H bond dissociation energy itself; and what would be expected even for formation of a classical radical may be considerably uncertain.

Thus, at least for the present, structural and energetic attributes must serve primarily to help us to picture the nonclassical species conceptually rather than to determine whether a given radical is or is not nonclassical.

Radicals are capable of direct observation via electron-spin reasonance spectroscopy. A principal result is information regarding the distribution of the odd electron. Nonclassical species are expected to show extensive hyperfine interactions with atoms at or near the possible centers of electron delocalization. Rapidly equilibrating classical radicals might show similar results for the time-average spin distribution. If so, it might be possible, as in nuclear magnetic reasonance spectroscopy, to freeze out and study individually one or more of the interconverting species by using low temperatures. Such an approach could in principle allow an unambiguous answer to the question of the nature of the radical intermediates.

In carbonium-ion chemistry, the special stability of nonclassical ions is often manifested by unusually high rates of formation via solvolysis of suitable precursors. However, sole use of kinetic criteria for the absence of nonclassical character can not ultimately be successful, because rates of formation relate not to the energy of the product radicals or ions but to that of transition states for their formation in which there is only partial radical or ionic character. The possibility can not be dismissed that the balance of factors which causes a radical or ion to opt for σ-electron delocalization is a delicate one in which a full free valency or a full charge deficiency may be required to tip the scales in favor of delocalization.

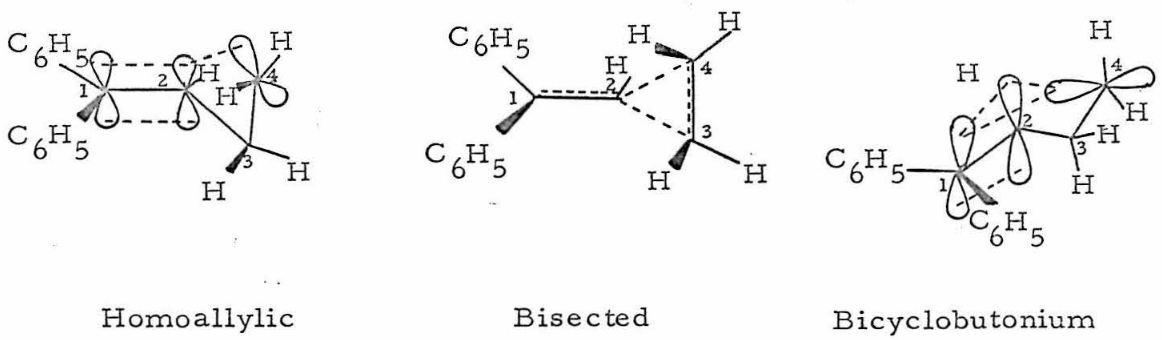
Finally, the nature of the radical intermediates in a given system can be probed mechanistically. A radical which has more than a single center of free valence has the possibility of taking up an atom such as hydrogen at alternative positions to give in general distinguishable products. In this work we have employed product studies as a function of reaction temperature and hydrogen-donor reactivity to obtain data which we feel can be used in part to distinguish between formation of two such products, ring-opened hydrocarbon **5** and ring-closed hydrocarbon **6**, from a common intermediate (**7**) or from a rapidly equilibrating pair of classical, single-product intermediates (**3** and **4**). We may *imagine* that an appropriate nonclassical radical represents a



structural compromise between the geometries of the classical ring-opened radical **3** and the classical ring-closed radical **4** and that it would be more stable than either, if it is to be the principal product-forming intermediate. But we shall be able to detect its presence only if it gives rise to appreciable amounts of both the isomeric hydrocarbons **5** and **6** on the limited hydrogen-donor diet we have been able to provide (see below).

Possible structures for nonclassical radical **7** are depicted in Chart 8. The homoallylic and bicyclobutonium structures are formally interconvertible by rotation about the C-2—C-3 bond, the difference being that C-4 is appreciably closer to C-2 than to C-1 in the former whereas these distances are comparable in the latter. Semi-empirical Hückel molecular orbital calculations (13a) suggest that strong 1, 4 and 2, 4 interactions are favorable in the analogous carbonium-ion intermediates (but with the phenyl groups replaced by hydrogens), where the orbital system sketched accommodates only two electrons, but that three electrons are better accommodated in the homoallylic-type structure. Moreover, the apparent lack of interconvertibility of cyclobutyl structures with allylcarbinyl and cyclopropylcarbinyl structures in free-radical reactions (15) is in striking contrast to the facile interconversion of structures of all three types in carbonium-ion reactions (14). This suggests that a homoallylic or bisected (see below) structure for **7** is more likely than a bicyclobutonium structure.

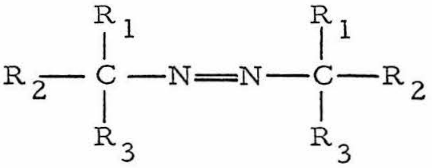
Chart 8. Possible Structures for Nonclassical Radical **7**.



Homoallylic Bisected Bicyclobutonium

A strong possibility for a favorable nonclassical structure for the cyclopropylcarbinyl radical has the so-called "bisected" geometry in which carbon atoms 3 and 4 are equivalent. The name comes from the fact that the plane containing C-1 and the three flanking carbon atoms is perpendicular to--bisects--that containing C-2, C-3, and C-4. Bisected geometries have been demonstrated experimentally for cyclopropanecarboxaldehyde (115a), cyclopropyl methyl ketone (115b), phenylcyclopropane (115c) and for cyclopropyl semidione radicals (115d). Perhaps more pertinent is that rather good evidence has been obtained, using methyl groups as a probe for charge delocalization, that transition states in cyclopropylcarbinyl solvolyses have the bisected geometry (116). The key point here is 3, 4-dimethyl-substituted compounds solvolyze at virtually the same rate as the 3, 3-dimethyl compound, and that each solvolyzes about 10 times as rapidly as the 3-methyl compounds (which in turn solvolyzes about 10 times as rapidly as the unsubstituted compound). If charge delocalization (which must apparently be invoked to account for the unusually high solvolytic rates of cyclopropylcarbinyl derivatives (116)) occurred as in the homoallylic or bicyclobutonium structures either to C-3 or to C-4, but not to both, the 3, 4-dimethyl-substituted compounds should solvolyze only about twice as rapidly as the 3-methyl-substituted compounds. By tying back C-3 and C-4 or C-2 and C-3 with methylene bridges of varying lengths (thus introducing varying degrees of ring strain), evidence was also obtained for the lengthening of the 2, 3 and 2, 4 bonds and the shortening of the 3, 4 bond implied by the dotted lines (116).

Moreover, kinetic measurements on rates of decomposition of azo compounds recently reported by Martin *et al.* (117) bear on the question of the origin of the well-known stabilization of a radical center by cyclopropyl groups (118). Martin studied a series of symmetrical azo compounds in which R_1, R_2, and R_3 were methyl groups and in which one, two, and all three methyl groups on each side were replaced by cyclopropyl groups. The first substitution of cyclopropyl for methyl increased the rate of decomposition (diphenyl ether, 135°) by a factor of 27. With two and three cyclopropyl groups on each side, relative rates were 362 and 2540. And finally, the compound with two cyclopropyl groups and one isopropyl group in each half was found to decompose 286 times as rapidly as the hexamethyl compound.



$$\mathrm{R_2-\underset{R_3}{\overset{R_1}{C}}-N{=}N-\underset{R_3}{\overset{R_1}{C}}-R_2}$$

The significant factor is that repeated substitution of cyclopropyl for methyl continues to result in significant rate increases. The rate of decomposition of the tetracyclopropyldiisopropyl compound shows that this can not simply be due to increased steric strain in the azo compound which is relieved in the decomposition transition state. And if the mode of interaction were relief of strain by concerted opening of one cyclopropyl ring (to the allylcarbinyl form), only much smaller rate increases due to statistical factors should have resulted upon successive substitution. Apparently, any number of α-cyclopropyl rings can participate; an attractive possibility would be to have each take up a bisected conformation with respect to the radical center.

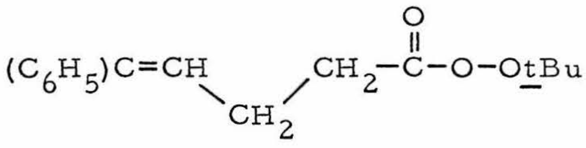
The evidence is that two radical species give rise to 5 and 6 at least at short times after the homolysis of a ring-closed precursor, and that one of these radicals behaves very much as we expect the classical ring-closed radical 4 should behave. It may well be that 4 has a bisected geometry and that investigation by electro-spin resonance spectroscopy or rigorous quantum-mechanical calculation would indicate 'significant' σ-electron delocalization into the cyclopropyl ring, as is implied by the use of dotted lines in representing the bisected form of 7. But it presently appears that the 'classical ring-closed radical' does not give ring-opened products upon hydrogen abstraction from 1,4-cyclohexadiene, triethyltin hydride, or cyclohexadienyl radicals, and by this criteria, at least, there is no evidence demanding it be nonclassical.

In most of what follows, we shall assume the homoallylic form whenever product formation from a nonclassical radical is under consideration. But we must admit the possibility that the 'classical ring-closed radical 4' may be best formulated--from a wave-mechanical viewpoint--as the bisected nonclassical radical 7.

For our purposes here, a radical such as 4 is operationally nonclassical only if it is observed to give multiple products. Different sets of experiments might yield different conclusions in this regard, as might fundamentally different approaches. However, in the absence of spin-resonance experiments or definitive quantum-mechanical calculations, definitional problems seem to be unavoidable. The concept of nonclassical character is therefore necessarily relative and imprecise.

2. Summary of Relevant Experimental Observations

This work was begun in the light of Howden's discovery that thermal decomposition of ring-opened perester 1 in the presence of tri-*n*-butyltin hydride gave ring-opened hydrocarbon 5 and ring-closed hydrocarbon 6 in sensibly constant proportions of 20:1 (21). His experiments covered reaction temperatures from 110 to 150° and initial tin hydride concentrations from 0.056 to 0.56 M (see Table 12, p. 44).



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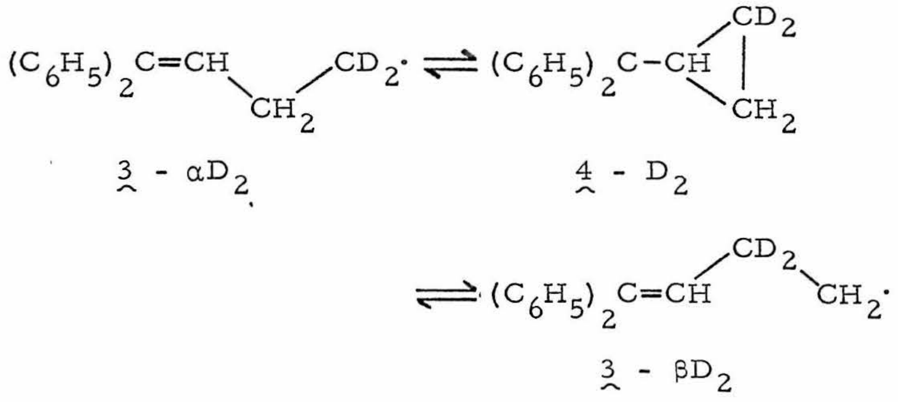
The insensitivity of the product ratio to the tin hydride concentration is interpretable in terms of product formation by the classical radicals 3 and 4, by a nonclassical radical such as 7, or in terms of any admixture of the two schemes; one has only to postulate rapid equilibration of all radical species which give rise to the isomeric hydrocarbons.

In contrast, the lack of an appreciable temperature effect was taken by Howden to tentatively and indirectly implicate a nonclassical radical, perhaps our 7, as the product-forming species. This inference was predicated upon his estimation, via a complex thermochemical cycle (119), that isomerization of ring-closed 4 to ring-opened 3 would be endothermic by 24.5 kcal/mole (21, 119). As the difference in activation energy for abstraction of hydrogen by the two radicals from a donor as reactive as tri-*n*-butyltin hydride (120) would not be expected to be of comparable magnitude, product formation from the classical radicals should evidently have been accompanied by a strong dependence of the ratio 6:5 on the reaction temperature.

As it happens, the large enthalpy difference estimated by Howden is due to an error of sign in the relationship between the heat of reaction and the enthalpies of the reactants and products (119).* However, at the time this work was begun either Howden's value or a value of 17 kcal/mole derived by us seemed to suggest that the classical radicals might interconvert too slowly to explain the insensitivity of the ratio 6:5 to tin hydride concentration.

The possibility of interconversion can easily be tested by examining products from the decomposition of deuterium-labeled 1 for the position of the label. The minimum requirement for the implication of rapidly equilibrating classical radicals 3 and 4 was attained when



3 - αD_2

4 - D_2

3 - βD_2

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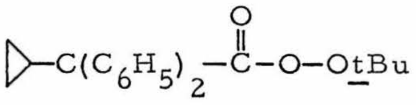
[*] One commonly writes equations such as A⟶B + ΔH, where ΔH is the heat of reaction. This erroneously suggests the relationship $\Delta H_f(\text{reactants}) = \Delta H_f(\text{products}) + \Delta H_{rxn}$. The unnatural, but correct, equation has a minus sign.

complete scrambling was found, within experimental error, in appropriate reaction products for decomposition of labeled 1 in cyclohexane and in 1.3 M triethyltin hydride in *n*-octane (pp. 94–96).

Using triethyltin hydride in place of Howden's tri-*n*-butyltin hydride, we were able to confirm the lack of any appreciable effect of the tin hydride concentration on the ratio of 6:5 at 125 and 144°. At 10 and 35° using the more reactive ring-closed perester 2, however, an



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experimentally significant dependence of the product ratio on the tin hydride concentration was found (see Fig. 8, p. 100). This observation immediately requires that any proper mechanistic scheme advance at least two product-forming intermediates, but leaves open the question of their nature.

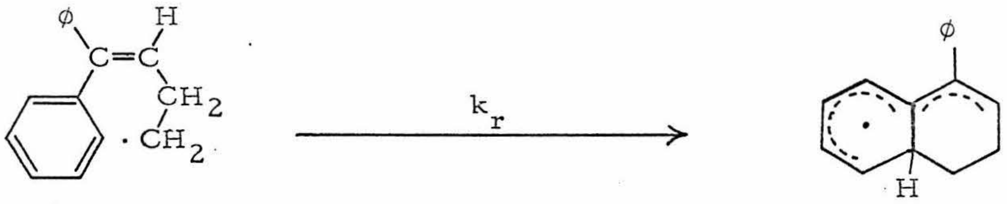
Evidence of another sort may be cited to similar effect. The cage-reaction products which result from decomposition of the isomeric peresters apparently have the ring-opened structure when the perester is ring-opened but the ring-closed structure when the perester is ring-closed (subsection 5 to Section One).

From Howden's vantage point, product formation solely from a nonclassical radical such as 7 not only promised to explain the lack of a hydrogen-donor concentration effect and the small temperature effect on 6:5, but also had a certain elegance of simplicity to recommend it. Given the existence of at least two product-forming free-radical intermediates, a proper respect for such considerations would now appear to favor an interpretation based on the classical radicals.

Such is indeed our conclusion, subject to the definitional problems discussed in the previous subsection. We shall proceed in this subsection to consider additional experimental support for this conclusion and to show via an energy-level scheme that our results in this regard are nicely explicable on the assumption that we are dealing with two intermediates, one of which gives ring-opened product and the other of which gives ring-closed product. Strictly speaking, the trapping results and the cage-product results do not however rule out the possibility that initially formed classical radicals isomerize to a nonclassical species and that ratios of **6**:**5** formed under conditions which permit prior equilibration of the radical intermediates represent essentially the partitioning of such a species to ring-closed and ring-opened product. We have therefore advanced what we feel to be good, if somewhat complex, arguments which are intended to show that such an interpretation is fraught with serious difficulties. Some readers may feel that such arguments are unnecessary--that the self-consistency and reasonableness of the classical-radical interpretation is itself sufficient to establish that interpretation. That self-consistency is further explored in subsection 4, where the energy-level scheme constructed here is extended to one offering absolute rate-constant estimates, the purpose in part being to show that experimentally inferred values of various composite parameters (rate-constant ratios, etc.) do not conceal unreasonable implications. And finally, in subsection 5 we employ a thermodynamic cycle to show that an inferred difference in enthalpy of ring-opened radical 3 and ring-closed radical 4 (see below) is reasonable.

On the presumption that the radical intermediates are ring-closed 3 and ring-opened 4, it is possible to deduce from the intercepts of plots of 6:5 against the tin hydride concentration at 10 and 35° and from values of this ratio observed at 110 and 125° that the transition state for formation of 6 from 4 lies 2.9 ± 0.3 kcal/mole below that for formation of 5 from 3 (see Fig. 9, p. 103). Thus, the small temperature effect which eluded Howden is easily discerned here with our wider temperature range. In addition, the difference in the slopes of the plots of 6:5 against the tin hydride concentration at 10 and 35° was found to imply that the transition state for interconversion of 3 and 4 lies 4.6 ± 0.7 kcal/mole above that for formation of 6 from 4 and 1.7 ± 0.8 kcal/mole above that for formation of 5 from 3. These relationships, originally traced on the reaction diagram, Fig. 10, p. 105, are preserved here in the final diagram, Fig. 23, p. 333.

It was also possible to obtain Arrhenius relationships for the rate-constant ratio which describes, in the present interpretation, the partitioning of ring-opened radicals between ortho-ring cyclization (k_r) and hydrogen abstraction from 1,4-cyclohexadiene and from triethyltin hydride ($k_a^{\bigcirc}$ and k_a^{SnH}) (eq. 2.4-22, p. 272, and eq. 1.8-11, p. 138).



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Elimination of the k_r reference process gave (eq. 1.8-12, p. 138):

$$k_a^{\mathrm{SnH}}/k_a^{\text{⬡}} = 0.7\,\exp(+3.2/RT) \quad . \qquad (3.2\text{-}1)$$

The estimated uncertainties in the activation energies for the precursor eqs. 1.8-11 and 2.4-22 give an estimated standard error of $(0.7^2 + 1.0^2)^{\frac{1}{2}} = 1.2$ kcal/mole in the activation of eq. 3.2-1.

Construction of a semiquantitative scheme such as Fig. 23 depicting absolute, rather than simply relative, activation energies requires the measurement or the estimation of an absolute activation energy for one reaction of each of the two radicals. Not being equipped to measure absolute rate constants, we must employ the second alternative. Accordingly, we have assumed that the activation energy for hydrogen abstraction by ring-opened radical 3 from 1,4-cyclohexadiene in hydrocarbon solution (the $k_a^{\text{⬡}}$ process) is equal to the literature value of 5.8 kcal/mole for hydrogen abstraction by the ethyl radical from the same donor, but in the gas phase (45).[*] As can be traced in Fig. 22, this assumption makes it possible to estimate activation energies of 2.6 kcal/mole for hydrogen abstraction by 3 from triethyltin hydride and of 4.3 kcal/mole for isomerization of ring-opened 3 to ring-closed 4.[**]

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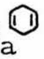
[*] See the discussion on p. 349 regarding the interpretation of the literature value.

[**] At this point it becomes difficult to continue to give reliable estimates for the uncertainty in relative energy-level placements. The estimated 2.6 kcal/mole for the activation energy of the k_a^{SnH} process may seem a bit low to some, but it is uncertain by 1.2 kcal/mole due to the standard error in $k_a^{\mathrm{SnH}}/k_a^{\text{⬡}}$ as well as by an undetermined amount due to any error in the assumed 5.8 kcal/mole activation energy for the $k_a^{\text{⬡}}$ process. Similarly, the radical-interconversion barrier could well be in error by as much as 2 kcal/mole.

No wonder the classical radicals are so hard to trap relative to their rate of interconversion.

The remaining energy-level placements were made on the basis of the mechanistic treatment of Section Two. From the temperature dependence of the ratio 6:5 for hydrogen abstraction from 1,4-cyclohexadiene (-1.8 ± 1.0 kcal/mole; heading I, p. 273), we can place the transition state for formation of **6** by this route at 4.0 kcal/mole in Fig. 23. We should caution, however, that an experimental complication prevents this from being an unambiguous result (heading I, p. 273).

The dominant routes to **5** and **6** for perester decomposition in 1,4-cyclohexadiene under most conditions employed have **3** reacting with cyclohexadiene but **4**, with cyclohexadienyl radical. It was possible to infer the relative energies of the respective transition states to within one kcal/mole (heading K, p. 277). The inference places the transition state for **4** plus cyclohexadienyl radical at 5.8 - 11.6 = -5.8 kcal/mole (Fig. 22, p. 279).

If we also assume a viscosity-related 'activation energy' for disproportionation of **4** with cyclohexadienyl radical of 2 kcal/mole arising from the lesser impedence to diffusion at higher reaction temperatures (hence lower solution viscosities), we can estimate the isomerization of ring-opened **3** to ring-closed **4** to be exothermic by ~8 kcal/mole. The uncertainty in the above assumption and that in the assumed activation energy for the k_a process combine to make the heat of isomerization uncertain by perhaps 3 kcal/mole (heading K, p. 277), but do not effect the conclusion that **4** is considerably the more stable (as regards enthalpy).

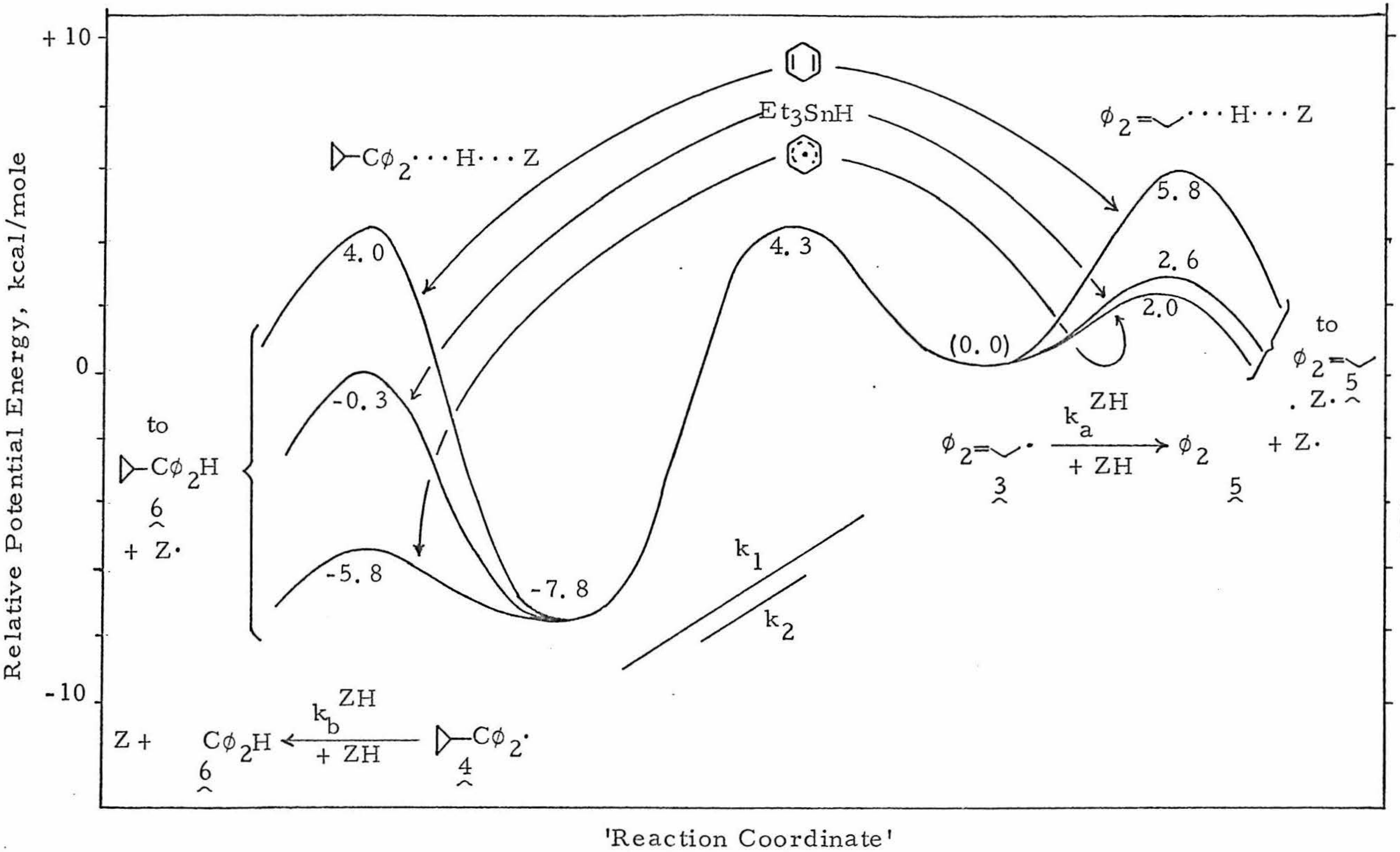


Figure 23. Semi-quantitative reaction diagram for ring-opened radical 3 and ring-closed radical 4 in the presence of 1,4-cyclohexadiene, triethyltin hydride, and cyclohexadienyl radical. Numbers shown are energy-level placements in kcal/mole relative to assumed energy zero for 3. See Figs. 10, 11, 13, and 22 for construction of the scheme.

To complete the picture, we again assume a 2 kcal/mole viscosity-related activation energy for disproportionation of ring-opened radical 3 with the cyclohexadienyl radical. The difference of about 8 kcal/mole in the transition-state energies for reaction of 3 and 4 with cyclohexadienyl radical should result in a large temperature dependence for the characteristic ratio of 6:5 formed in this way.* However, the ratio itself is sufficiently large (probably greater than 5 at 100°) that the relevant data do not yield more than a minimum value (heading J, p. 275). By way of comparison, the characteristic ratio at 100° for hydrogen abstraction from triethyltin hydride is calculated from eq. 1.7-5 to be 0.078, whereas that for hydrogen abstraction from 1,4-cyclohexadiene is estimated to be 0.0035 ± 0.001 (heading I, p. 273).

Ratios of such quantities yield the relative effect of substitution of one hydrogen donor for a second on the rate constants for hydrogen abstraction by 3 and 4. We can, however, isolate the effect of a hydrogen-donor change on rate constants for the former (the k_a processes) by combining rate-constant ratios for hydrogen abstraction to *ortho*-ring cyclization. Such a procedure gave us eq. 3.2-1, from which we find that at 100° ring-opened radicals abstract hydrogen from triethyltin hydride approximately 50 times more rapidly than from 1,4-cyclohexadiene for equal hydrogen-donor concentrations. On the

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*The characteristic ratio of 6:5 for abstraction of hydrogen from ZH is given by $k_1k_b^{ZH}/k_2k_a^{ZH}$. See Fig. 23 for definitions of the individual rate constants.

same basis, abstraction from indene is approximately a factor of 5 slower than from 1,4-cyclohexadiene (p. 125).[*]

We can now infer from the characteristic-ratio comparison that ring-closed radicals abstract hydrogen more rapidly from triethyltin hydride than from 1,4-cyclohexadiene by a factor of 0.078 × 50/0.0035 $\cong$ 1000 at 100°. The relative rate of hydrogen abstraction by 4 from the cyclohexadienyl radical can be fitted into this scheme via an indirect comparison. Thus, the assumption that ring-opened radicals abstract

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[*] Literature reports (45, 54) recapitulated here as eq. 1.8-9, p. 127, show hydrogen abstraction by ethyl radicals in the gas phase at 100° to be more rapid from 1,4-cyclohexadiene than from cyclohexane by a factor of 260. An analogous comparison for hydrogen abstraction by saturated primary radical 21 in solution gives, perhaps fortuitously, a nearly identical value of 250 at 100° when corrected from 152° by a factor of 2.0 using the activation energy quoted in eq. 1.8-9 for ethyl radical reactivities.[**] Thus we have the following scale of relative reactivities toward hydrogen abstraction by primary radicals: cyclohexane, 0.004; indene, 0.2; 1,4-cyclohexadiene, 1.00; triethyltin hydride, 50. We are prompted to offer this reactivity series by the apparent lack of such comparisons for abstraction by hydrocarbon radicals from hydrogen donors greatly more reactive than cyclohexane.

[**] Assuming an efficiency of conversion of the saturated ring-cyclized radical 24 to 1-phenyltetralin 25 of 40% (see p. 141 and heading P, p. 286, for justification), entries in the rightmost column of data Table 3 for rows 2–5 give a rate constant ratio of 0.54 for the partitioning of saturated radicals 21 between cyclization to 24 and abstraction of hydrogen from 1,4-cyclohexadiene to give saturated hydrocarbon 20. The analogous ratio where the hydrogen donor is cyclohexane may be estimated as 67 using results in row 1 of Table 3. To get this estimate we assume that the 73% of products not accounted for by 20 plus the cage products 18 and 19 (p. 82) represent saturated radicals 21 which underwent ring-cyclization to 24 and rearrangement via spiro closure to 27 in the proportion of 1.5:1 (see p. 143). Thus, total conversion of 24 to 25 would have given a yield of 25 of 73 × 1.5/2.5 = 44% as compared to the observed yield of 19.6%. Combining the former with the 5.1% observed yield of 20 and the estimated concentration of cyclohexane at 152° of 7.8 M (see footnote c to Table 3) as in eq. 1.8-5, p. 111, then gives a partitioning ratio of 44 × 7.8/5.1 = 67. The factor of 250 is then obtained as 67 × 2.0/0.54.

hydrogen with equal facility from triethyltin hydride and from the cyclohexadienyl radical implies that ring-closed radicals prefer the latter over 1,4-cyclohexadiene by a factor of $1000 \times 5/0.078 = 65000$. This is of course a minimum value; the actual figure is probably close to 10^9.[*] Thus the reactivity sequence for hydrogen abstraction by 4 is roughly: 1,4-cyclohexadiene, 1.00; triethyltin hydride, 10^3, cyclohexadienyl radical, $\geq 10^6$.

The pattern is clear: the more reactive the hydrogen donor, the larger the characteristic ratio of 6:5. This result is easily rationalized, assuming the classical radicals to be the product-forming species, as a radical-chemistry example of the usual reciprocal relationship between stability and reactivity. A hydrogen donor in effect constitutes a radical counter. A relatively unreactive hydrogen donor such as 1,4-cyclohexadiene is so predisposed to react with ring-opened radicals that it produces more of the product from 3 than from 4. Cyclohexadienyl radicals, on the other hand, are sufficiently undiscriminating that they do favor the product from the most prevalent radical. Still, they fail to demonstrate the large magnitude of the equilibrium constant which--we shall argue in subsection 4--favors 4 over 3 by factors of roughly 9×10^2 at 100° and of 4×10^4 at 0°.

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[*] This, at least, is the value given by the absolute rate-constant scheme of subsection 4.

3. Attempted Reinterpretation in Terms of a Nonclassical Radical

The utterly different natures of the cage-reaction products from ring-opened perester 1 and ring-closed perester 2 and the dependence of the ratio 6:5 on the concentration of triethyltin hydride at 10 and 35° confirm the existence of at least two kinds of product-forming radical intermediates. The cage-reaction products also show that one radical intermediate gives largely or wholly ring-opened product and that a second gives largely or wholly ring-closed product. These would presumably be ring-opened 3 and ring-closed 4. However, it is still possible that at sufficiently long times a third species (e.g., nonclassical homoallylic radical 7) assumes control of product formation and that the characteristic ratios 6:5 represent the partitioning of such a species between ring-closed and ring-opened product. Let us suppose that this is the case and see what conclusions can be reached.

We have noted in subsection 2 that hydrogen abstraction from cyclohexadienyl radical gives 6:5 in the ratio of at least 5:1 at 100°. Let us assume, for the sake of argument, that a donor which reflects precisely the distribution of free valence at the dibenzylic and the terminal primary carbons of 7 gives 6:5 in a ratio of 10:1; i.e., that the ratio of preexponential factors for formation of 6 and formation of 5 is 10:1. If this same preexponential-factor ratio is assumed for the real hydrogen donors (cyclohexadienyl radical, triethyltin hydride, and 1,4-cyclohexadiene), the reaction diagram scheme for formation of 5 and 6 would resemble that of Fig. 24.

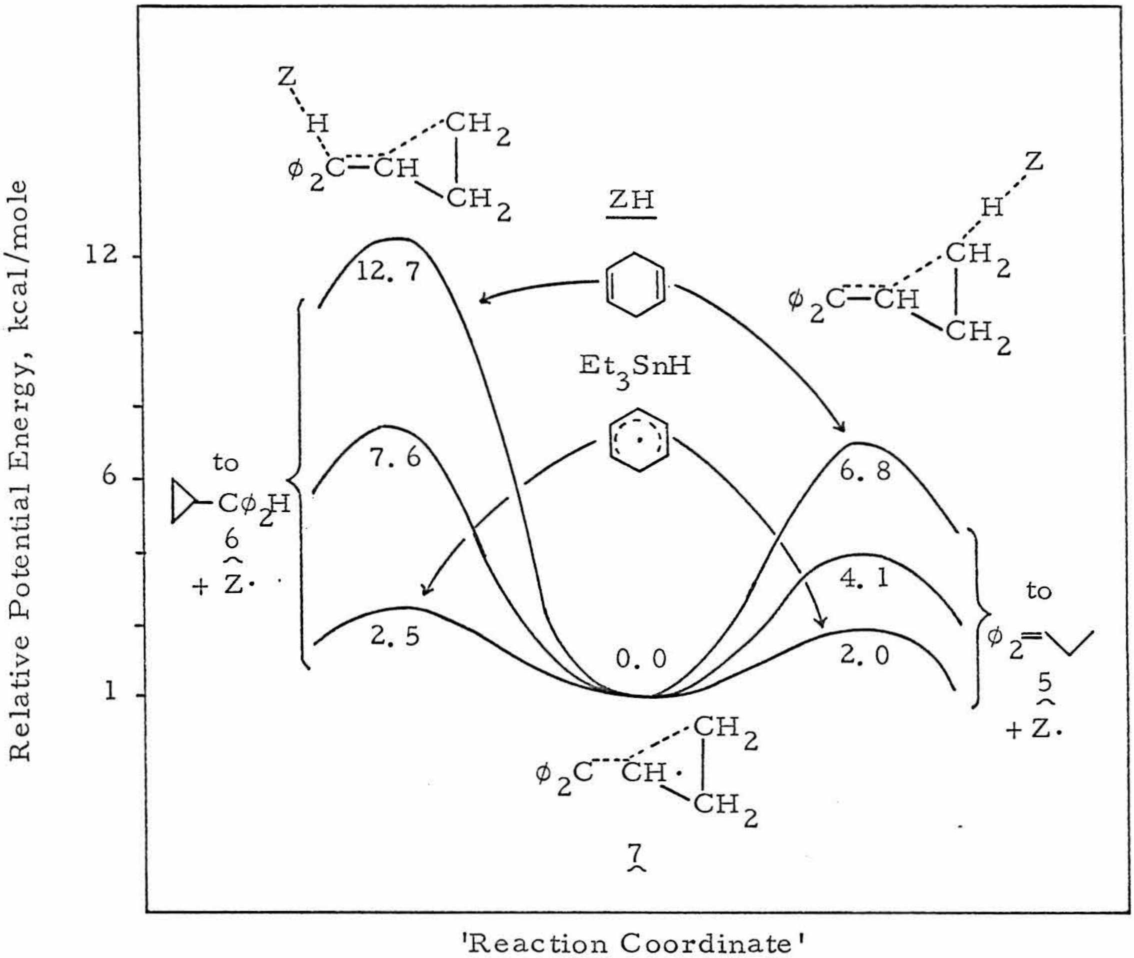

Figure 24. An energy-level diagram for product formation by non-classical homoallylic radical 7 constructed to fit observed ratios of 6:5 at 100°.

In placing the energy levels in Fig. 24 we have employed the observed characteristic ratios at 100°, an assumed activation energy of 2.0 kcal/mole for formation of 5 from 7 plus cyclohexadienyl radical, and the relative rate ratios of 1:1000:~10^6 inferred in subsection 2 for hydrogen abstraction to give 6 from 1,4-cyclohexadiene, triethyltin hydride, and cyclohexadienyl radical. The last point, it should be noted, is valid whether the radical giving 6 is the classical radical 4 or is 7.[*]

Note that the dependence of the abstraction barriers on each side on the reactivity of the hydrogen donor is very similar to the behavior seen in Fig. 23. This of itself is most reasonable. However, the characteristic ratio 6:5 is now predicted to universally increase with increasing temperature. This is grossly incorrect. For abstraction from triethyltin hydride, the observed characteristic ratios are 0.29 at 10°, 0.16 at 35°, 0.07 at 110°, and 0.06 at 125° (Fig. 9, p. 103). The scheme also gives a greatly different temperature dependence than was inferred with but slight reservation for hydrogen abstraction from 1,4-cyclohexadiene (heading I, p. 273). Moreover, it directly contradicts the conclusion reached in Section Two (heading K, p. 277) that the transition state for formation of 6 via hydrogen abstraction from cyclohexadienyl radicals lies ~12 kcal/mole below that for formation of 5 from 1,4-cyclohexadiene.[**]

Thus we have in Fig. 24 a scheme which would be reasonable *a priori*, but which fails to account for the actual product-ratio observations. The obvious next approach is to construct an energy-level scheme which does account for the observations and to ask whether the properties it requires of nonclassical radical 7 are reasonable ones.

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[*] Moreover, the *relative* placement of the hydrogen abstraction transition states for *a given* donor does not require the assumption of any such reactivity series.

[**] We shall show shortly that the revised definitions of the arabic-letter parameters of eqs. 2.1-4 are just such that the composite quantity on the left-hand side of eq. 2.4-25, p. 277, again specifies the enthalpy difference of these two transition states.

Our first task is to determine what the mechanistic scheme of Section Two requires of a nonclassical radical, if that species alone is to account for formation of ring-opened hydrocarbon 5 and ring-closed hydrocarbon 6 in the observed amounts. This simply amounts to working out the new interpretations of the arabic-letter parameters of eqs. 2.1-4; we already have deduced their values (Table 19, pp. 303 - 307). The new reaction steps we shall consider are shown in Chart 9; these replace analogous steps based on classical radicals which occupy essentially the lower-left quadrant in Chart 7, p. 198. We consider two possibilities: SCHEME A in which *ortho*-ring-cyclization to the radical 9 is again attributed to ring-opened radical 3; and SCHEME B in which the nonclassical radical 7, perhaps in the bicyclobutonium configuration of Chart 8 (p. 322), is assumed to give 9 directly. The new definitions of the affected parameters are given in Chart 9; the others are again as in eqs. 2.1-4, p. 203, except for C, which would change in an obvious way if we were to substitute reaction of 7 with 9 for that of the minor reaction of 4 with 9 of Chart 7. We shall leave it to the interested reader to confirm the redefinitions.*

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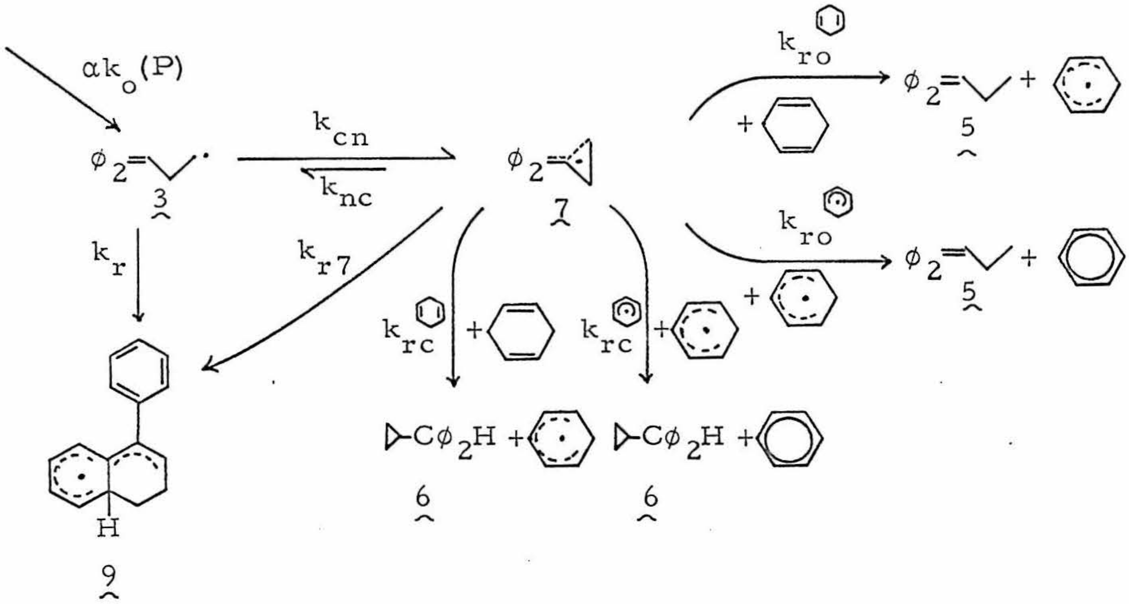
*This may be done for SCHEME A by updating eq. B3 of Appendix B and replacing eq. B4 for d(4)/dt by the appropriate equation for d(7)/dt. Adding these equations together gives the equation which replaces eq. B8. The assumption of rapid interconversion of 3 and 7 then allows eq. B9 to be updated. Comparison of the original and revised eqs. B9 to eq. 2.1-9, p. 206, yields the new definitions for E, G, H, and I. The procedure for SCHEME B is similar except that the concentration of 3 drops out upon addition of the revised eqs. B3 and B4. The result is directly the revised eq. B9 and comparison again yields the new parameter definitions.

A bit more work may, however, be required for the reader to convince himself that deployment of the new parameter definitions leaves the final forms of all other mechanistic equations invarient.

Chart 9. Some relationships for product formation by a nonclassical radical.



SCHEME A: $k_{r7} = 0$

$$E = \frac{k_{cn} k_{ro}^{⬡}}{k_{nc} k_r} \qquad G = \frac{k_{cn} k_{rc}^{⊙} k_3^{\frac{1}{2}}}{k_{nc} k_r k_d}$$

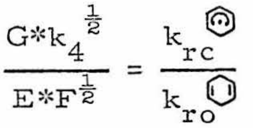
$$H = k_{rc}^{⊙} / k_{ro}^{⊙} \qquad I = k_{rc}^{⬡} k_{ro}^{⬡}$$

SCHEME B: $k_r = 0$

$$E = k_{ro}^{⬡} / k_{r7} \qquad G = \frac{k_{rc}^{⊙} k_3^{\frac{1}{2}}}{k_{r7} k_d}$$

H, I: as in SCHEME A

Note that the activation energy of the parameter I, evaluated as -1.8 ± 1 kcal/mole, is again the energy of the transition state for formation of 6 via abstraction from 1,4-cyclohexadiene less that for formation of 5 from the same donor. And the composite quantity



$$\frac{G^*k_4^{\frac{1}{2}}}{E^*F^{\frac{1}{2}}} = \frac{k_{rc}}{k_{ro}}$$

(for SCHEME A or B)

on the left-hand side of eq. 2.4-25, p. 277, again relates the transition-state energies for formation of 6 via hydrogen abstraction from cyclohexadienyl radical and formation of 5 via abstraction from 1,4-cyclohexadiene. All of this is to say what experienced observers will have already recognized: relationships between transition-state energies for formation of products which were placed with cause in Fig. 23 are unaffected by any reformulation having to do with the nature of the radical intermediates which give rise to the hydrocarbon products, so long as rapid equilibration of all such species is again presumed. Thus, we can compile Fig. 25 simply by deleting central hump in Fig. 23 and stitching the two sides together. The only exception is the transition state for formation of ring-opened material via hydrogen abstraction from cyclohexadienyl radical; that placement was not originally made with cause, but rather in the expectation that the activation energy would be minimal. The same assumption now gives a radically different level placement.

Thus we now have a scheme which accounts for the observed temperature dependencies of the characteristic ratios for hydrogen

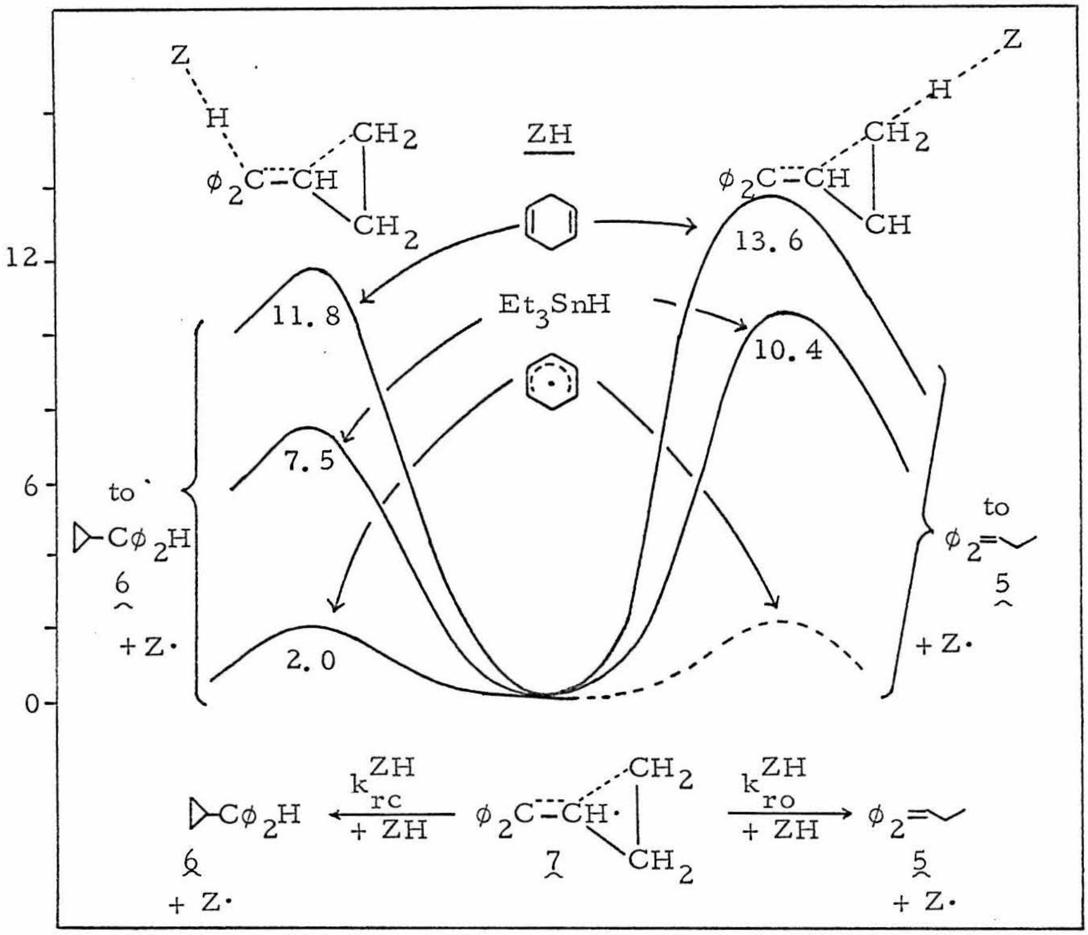


Figure 25. An energy-level diagram for product formation by nonclassical homoallylic radical 7 constructed to fit the observed dependence of ratios of 6:5 on the reaction temperature.

abstraction from 1,4-cyclohexadiene and triethyltin hydride. We now ask whether the scheme is reasonable in other respects. A first point concerns the location of the lower barrier on the right in Fig. 25. Let us first assume that reaction of 7 with cyclohexadienyl radical to give ring-opened material requires a minimal activation energy, as shown in the figure. We must then conclude from the fact that the same donor gives principally ring-closed material (H > 5 at 100°)* that the preexponential factor for $k_{rc}^{\odot}$ exceeds that for $k_{ro}^{\odot}$, perhaps by a factor of 10 or so. However, by combining the relative transition-state energies for triethyltin hydride and for 1,4-cyclohexadiene with the characteristic ratios observed at 100° (0.078 and 0.0035, respectively) we can infer the analogous ratios of preexponential factors to be 4×10^{-4} and 1.5×10^{-3}, respectively. As the configurations around the methylene groups in the cyclohexadienyl radical and in 1,4-cyclohexadiene must be virtually indistinguishable, we must apparently attribute the difference of approximately 10^4 in the inferred preexponential factor ratios for these donors to the different natures of the abstraction processes (one being a radical-radical disproportionation), if we are to judge the scheme to be reasonable. The writer does not find so large a difference to be believable.

Moreover, the inferred ratio of preexponential factors for abstruction from 1,4-cyclohexadiene seems itself suspect. As we can show that the classical radical 4 should be energetically more stable than the ring-opened classical radical 3 (see subsection 5), we should expect any hybrid species to more closely resemble the former regarding the distribution of the free valence. We therefore expect in the

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*In deriving this value for H(100°) we have assumed the composite activation energy of -8 kcal/mole reflected in Fig. 22. This parameterization gives H(70°) = 2.5 H(100°) and H(0°) = 52 H(100°). Because significant yields of 6, the radical-radical product from 4, are formed only at 0° to 70° for decomposition of ring-opened perester 2 (compare yields of 6 in Tables 1 and 2), these would seem to be the experiments which determine the minimum acceptable value of H. If H had been required to be independent of temperature, we would expect to have found a value substantially larger than quoted here; thus, the argument given here would be reinforced. 23

absence of steric factors that the ratio of preexponential factors should favor the formation of ring-closed material. Thus, the steric factor favoring formation of ring-opened material must be considerably larger than $1/(4 \times 10^{-4}) = 2500$. This does not seem to be a readily acceptable inference.

Suppose we attempt at least partially to circumvent these difficulties by placing the barrier for formation of ring-opened material via hydrogen abstraction from cyclohexadienyl radical just below that for abstraction from triethyltin hydride. Then we arrive at the amazing conclusion that increasing the activity of the hydrogen donor benefits less the process of higher activation energy. Furthermore, regardless of where we place this barrier, it seems incongruous that the substitution of triethyltin hydride for 1,4-cyclohexadiene should favor formation of ring-closed material, by the observed factor of 20 (at 100°) or any other, if formation of the ring-opened material requires the greater activation energy for abstraction from 1,4-cyclohexadiene.

Another pair of points concerns the <u>ortho</u>-ring cyclization process. The tip of the activation barrier for that process would appear at 13.6 + 0.8 = 14.4 kcal/mole above our energy zero, since the composite activation energy for E is -0.8 kcal/mole (heading H, p. 272). If we assume that the nonclassical radical undergoes the cyclization, we infer an activation energy of ~14 kcal/mole. As we previously showed that <u>ortho</u>-ring cyclization by **3** should be more exothermic than isomerization of **3** to the classical radical **4** (heading Q, p. 287), it is apparent that ring-cyclization by **7** can not be greatly endothermic and would probably be exothermic or thermoneutral. This circumstance is hard to reconcile with an activation barrier of 14 kcal/mole.

We might then prefer SCHEME A, where the classical ring-opened radical is retained to account for the ring cyclization. But if 3 can undergo ring cyclization, presumably it can also abstract hydrogen to give ring-opened hydrocarbon 5. We have already investigated this question with reference to the partitioning between the two kinds of processes for the saturated radical 21 (heading B, p. 138). We found that formation of saturated hydrocarbon 20 occurs in 1 M 1,4-cyclohexadiene at a rate relative to ring cyclization to 24 which is a factor of 16 higher than the analogous rate-ratio for formation of ring-opened hydrocarbon 5 and ring-cyclization to 9 (pp. 140, 150). We concluded that a difference of this magnitude could simply be ascribed to a decrease in the rate constant for ring cyclization by 21 compared to that for cyclization by 3 owing (a) to a smaller activation barrier for cyclization by 3 arising from the greater delocalization of the odd electron in 9 (pp. 145–150) and (b) to the requirement for the freezing out of rotation around two carbon-carbon single bonds in attaining the transition state for cyclization by the saturated radical 21 as compared to that of but one rotation for cyclization by 3 (p. 150).

On the other hand, if most of the ring-opened hydrocarbon 5 resulted from hydrogen abstraction by a nonclassical radical incapable of undergoing the ring-cyclization, the relative rate of formation of 5 to cyclization to 9 would appear anomalously high--the factor of 16 quoted above would appear anomalously low--with respect to expectations based solely on classical radicals. There is no reason to believe that the observed factor of 16 carries such an implication. As we must therefore judge that the observed yields of hydrocarbon 5 are well in line with what should result from hydrogen abstraction by classical ring-opened radical 3 in competition with its ring cyclization to 9, it seems incorrect to attribute ring cyclization, but not hydrogen abstraction, to 3.

The comparison of partitioning ratios for the saturated and unsaturated systems can not, of course, take into account the possibility that isomerization by 3 to a species such as 7 might proceed so rapidly and so completely in that direction that *no* products are formed from 3. Since some species must cyclize, this must again be SCHEME B, already found to be unattractive in part by virtue of its attribution of a 14 kcal/mole energy barrier for an essentially thermoneutral isomerization of 7 to 9.

Our conclusion is that a nonclassical radical such as 7 can not reasonably be the major precursor of the ring-opened and ring-closed hydrocarbons. Our route to this conclusion has admittedly involved elements of conjecture and speculation. In the final analysis, we can hardly advise Nature that she must restrict the behavior of a nonclassical radical species within the narrow limits of the expectations expressed in this subsection. However, if our conclusion is incorrect, if a radical such as 7 predominates once the species most faithful to the patterns of bonding in the starting peresters have retired, then such a species must behave very remarkably indeed.

4. Absolute Rate Constant Estimates

In subsection 2 we considered an approximate energy-level scheme for interconversion of and hydrogen abstraction by the classical radicals 3 and 4. That scheme can be extended with but little more work to one affording absolute rate-constant estimates.

There are several reasons for the presentation of such a scheme. One is that only in this way can we show that the values found for composite parameters such as E, G, H, and I do not conceal unreasonable implications. We suggested in subsection 3 that interpretation of such quantities in terms of product formation principally from a nonclassical radical results in several apparent inconsistencies. It seems only fair to put the classical-radical interpretation to a similarly demanding test. Moreover, we shall be able to estimate the equilibrium constant for the ring-opened and ring-closed radicals 3 and 4 instead of having to settle for the heat of interconversion alone. We shall also now be able to suggest time scales for the successive mechanistic levels (cage processes, radical equilibration, ring-cyclization) which were employed as an organizational basis in Section One.

A. The Estimation Procedure

We shall first give the rate-constant estimates and shall then note how they were obtained:

k_a $= 2 \times 10^{9} \exp(-5.8/RT)\ M^{-1}\ sec^{-1}$ (3.4-1)

$k_1 = 1 \times 10^{11} \exp(-4.3/RT)\ sec^{-1}$ (3.4-2)

$k_r = 4 \times 10^{10} \exp(-6.6/RT)\ M^{-1}\ sec^{-1}$ (3.4-3)

$k_a^{SnH} = 1.4 \times 10^{9} \exp(-2.6/RT)\ M^{-1}\ sec^{-1}$ (3.4-4)

k_b $= 3 \times 10^{10} \exp(-2.0/RT)\ M^{-1}\ sec^{-1}$ (3.4-5)

$k_2 = 4 \times 10^{12} \exp(-12.1/RT)\ sec^{-1}$ (3.4-6)

$k_b^{SnH} = 1 \times 10^{8} \exp(-7.5/RT)\ M^{-1}\ sec^{-1}$ (3.4-7)

k_b $= 2 \times 10^{7} \exp(-11.8/RT)\ M^{-1}\ sec^{-1}$ (3.4-8)

k_a $= 2 \times 10^{11} \exp(-2.0/RT)\ M^{-1}\ sec^{-1}$ (3.4-9)

Our point of departure is eq. 1.8-8 (p. 127), the ratio of the rate constant for hydrogen abstraction in the gas phase by ethyl radicals from 1,4-cyclohexadiene divided by the squre root of the rate constant for pairwise reaction (combination plus disproportionation) of ethyl radicals (45). The latter rate constant is reported by Shepp and Kutschke (46) to have an average value of $2 \times 10^{10}\ M^{-1}\ sec^{-1}$ in the temperature range 50–100° with an apparent activation energy of 2 ± 1 kcal/mole. In view of the reports that combinations of methyl radicals (47), of isopropyl radicals (48), and of t-butyl radicals (49) require no activation energy, we shall take pairwise reaction of ethyl radicals to have a rate constant of $2 \times 10^{10}\ M^{-1}\ sec^{-1}$, independent of temperature. This gives, in conjunction with eq. 1.8-8,

$$k = 2.5 \times 10^{8} \exp(-5.8/RT) \qquad (3.4\text{-}10)$$

for hydrogen abstraction from 1,4-cyclohexadiene by ethyl radicals.

The problem now is to relate this vapor-phase rate constant to that for the same process in hydrocarbon solution. The phase change per se will probably not much affect the activation energy, but many lines of reasoning suggest that preexponential factors for nonpolar processes may be expected to increase on going to the liquid phase by factors of perhaps 4 to 50 (121). This theoretical expectation has only recently become directly testable; Sauer and Ward have reported that addition of a hydrogen atom to benzene at 25° occurs with a rate constant of 3.7×10^7 in the gas phase, but 1.1×10^9 in water (111). This rate increase for the condensed phase process of a factor of 30 is close to the factor of 26 they report for addition of a hydrogen atom to toluene (111).

In writing eq. 3.4-1 for $k_a^{\bigcirc}$, we have adopted a rate increase of a factor of eight over eq. 3.4-10. This factor is meant to include a rate increase for going to the condensed phase plus a smaller rate decrease for substituting the relatively ungainly ring-opened radical $\underset{\frown}{3}$ for the compact, easily accessible ethyl radical as the hydrogen abstractor. Obviously, great precision is not attainable here, but we feel that eq. 3.4-1 should at least be of the correct order of magnitude.

We now readily obtain estimates for k_1 using eq. 2.4-5 (p. 253), for k_r using eq. 2.4-22 (p. 272), and for k_a^{SnH} using eq. 3.2-1.

To estimate k_2 and the k_b processes, we first recall eq. 2.4-25:

$$\frac{G^*k_4^{\frac{1}{2}}}{E^*F^{\frac{1}{2}}} = \frac{k_1 k_b^{\circledcirc}}{k_2 k_a^{\bigcirc}} \quad . \qquad (3.4\text{-}11)$$

Values of E, F, and G are available from Table 19, and k_4, the rate constant for pairwise reaction of cyclohexadienyl radicals, has been reported by Sauer and Ward (111) to be 1.8×10^9 M^{-1} sec^{-1} in aqueous solution at 25°. They also report a rate constant of $2-5 \times 10^{10}$ for the same process in the gas phase, a factor of 10 or more higher than in solution. In contrast, addition of a hydrogen atom to benzene or to toluene in the gas phase proceeded about a factor of 30 more slowly than in solution. Thus, pairwise reaction of cyclohexadienyl radicals is a diffusion-controlled process. As such, k_4 may obey Debye's eq. 2.4-7, p. 255, which anticipates a reciprocal relationship between a rate constant and the solution viscosity. Pertinent viscosity values are 1.00 centapoise at 20° for water and 0.96 centapoise for cyclohexane (106). If we assume a viscosity-related activation energy of 2 kcal/mole for k_4 (96) and employ values for E, F, and G obtained in 'most-representative' calculation number 14 (p. 305), we find that the left-hand side of eq. 3.4-11 has a value of 2.0×10^6 at 100° and a composite activation energy of -11.6 kcal/mole. Thus, we have that

$$\frac{k_1 k_b^{\text{⏣}}}{k_2 k_a^{\text{⌬}}} = 0.3 \exp(11.6/RT) \quad . \qquad (3.4\text{-}12)$$

Combining eqs. 3.4-12 and 2.4-5 (p. 253), we obtain

$$k_b^{\text{⏣}}/k_2 = 7 \times 10^{-3} \exp(10.1/RT)\ M^{-1} \quad . \qquad (3.4\text{-}13)$$

We already have in eq. 1.7-4 (p. 101) the analogous equation for k_b^{SnH}/k_2, and by combining eqs. 2.4-23 (p. 275) and 2.4-5 we obtain the analogous equation for $k_b^{⌬}/k_2$:

$$k_b^{\mathrm{SnH}}/k_2 = 2.4 \times 10^{-5} \exp(4.5/RT)\ M^{-1} \qquad (3.4\text{-}14)$$

$$k_b^{⌬}/k_2 = 6 \times 10^{-6} \exp(0.3/RT)\ M^{-1} \qquad (3.4\text{-}15)$$

Thus we see that estimation of k_2 or of any one of the k_b suffices to determine the other three. We have chosen to estimate $k_b^{\odot}$, the rate constant for transfer of a hydrogen atom from cyclohexadienyl radical to ring-closed radical 4, in the expectation that it should not be greatly different from k_4, the rate constant for pairwise reaction of cyclohexadienyl radicals discussed above. In writing eq. 3.4-5, we have put $k_b^{\odot} = \frac{1}{2} k_4$, but physically this relationship corresponds to taking $k_b^{\odot}$ to be only a fourth as large as k_4; that is, if 4 could be distinguished from the cyclohexadienyl radical only by some chemically and kinetically insignificant factor (such as a remote isotopic label), we would have $k_b^{\odot} = 2\, k_4$ according to the convention employed in this thesis. The factor of 4 is intended to account for the presumptively more stringent orientation for reaction of 4 with cyclohexadienyl radical arising from the steric congestion about the radical center in 4.

Finally, we have chosen $k_a^{\odot}$ as in eq. 3.4-9 on the assumption that reaction of ring-opened radical 3 with cyclohexadienyl radical should be subject to decidedly less severe orientational requirements than reaction of ring-closed 4 with cyclohexadienyl radical.

We shall now comment briefly on the reasonableness of the rate-constant estimates.

We find for the relative concentrations of ring-closed 4 and ring-opened 3 at equilibrium:

$$\begin{aligned} K &= k_1/k_2 = 2.5 \times 10^{-2} \exp(7.8/RT) \qquad (3.4\text{-}16) \\ &= 4 \times 10^4 \quad \text{at } 0^\circ \\ &= 9 \times 10^2 \quad \text{at } 100^\circ \\ &= 1 \quad \text{at } {\sim}800^\circ \end{aligned}$$

Apparently, ring-closed radical **4** has both a lower enthalpy, by about 8 kcal/mole, and a lower entropy, by about 7 e.u., than ring-opened radical **3**. We shall argue in the following subsection that the estimated enthalpy difference is reasonable. The quantitative reasonableness of the entropy difference is not so easily judged, but we feel that a lower entropy for the ring-closed form is indicated by the orientational requirements for electron delocalization into the phenyl rings in **4** (probably partially offset by the near coplanarity required for conjugation of the phenyl rings with the double bond in **3**) and by the presence of a cyclopropyl ring in **4** but a double bond in **3** (e.g., the entropy of formation of propane is 7 e.u. higher than that of cyclopropane). In any case, the enthalpy difference dominates at temperatures employed in this work.

Next we note that the scheme gives steric factors of ~ 14 for triethyltin hydride and ~ 100 for 1,4-cyclohexadiene favoring hydrogen abstraction by ring-opened **3** over that by ring-closed **4**. Although we know of no pertinent literature data, we find these steric factors to be intuitively reasonable. The difference between triethyltin hydride and 1,4-cyclohexadiene is within previously quoted estimates of experimental error; e.g., assuming that eqs. 3.4-14 and 3.4-15 are correct near the center of the range of temperatures investigated experimentally (i.e., at ~80°), a difference of 5.3 kcal/mole in the composite activation energies, instead of the quoted 4.2 kcal/mole, would have resulted in identical steric-factor estimates.

Finally, we can construct the parameter H using the rate-constant estimates:

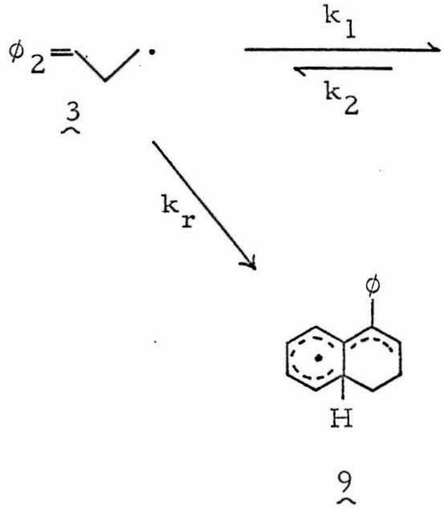
$$H = \frac{k_1 k_b^{\odot}}{k_2 k_a^{\odot}} = 4 \times 10^{-3} \exp(7.8/RT) \quad . \qquad (3.4\text{-}17)$$

Eq. 3.4-17 gives H(100°) = 100, which value is compatible with the roughly estimated lower limit of 5 obtained in Section Two (heading J, p. 275).

B. Characteristic Times for Cage Reaction, Radical Equilibration, and Ring-Cyclization

The mechanistic development in Section One was based on the concept of distinct time scales, or characteristic times, for the principal mechanistic levels which unfold sequentially before each C_{16} hydrocarbon radical between formation in a perester fragmentation and conversion to product. The shortest time period, we have said, is that during which the cage reaction products may be formed before diffusion separates the initial radical pair. If the hydrocarbon radical (at this stage ring-opened **3**, if the perester is ring-opened, or ring-closed **4**, if the perester is ring-closed) survives this stage, equilibration of the ring-opened and ring-closed forms of the radical, perhaps in competition with product formation via abstraction of hydrogen from a suitable donor becomes the principal order of business. In those cases where equilibration between 3 and 4 is attained before conversion to product occurs, the emphasis now shifts to competition between hydrogen abstraction and ring-cyclization to 9. Finally, if the latter occurs, conversion to nonradical products must usually await the appearance of a second radical species.

We shall give here semiquantitative estimates for the time scales of the first three levels. To do this we shall treat kinetically the abbreviated scheme of reactions shown below, where we shall take the



radical species born in an hypothetical perester decomposition to be ring-opened 3 and will ask at subsequent times for the probabilities that the radical is 3, 4, or 9.

The kinetic scheme depicted above leads to a pair of simultaneous first-order linear differential equations whose solution by the method discussed by Benson (122) is reasonably straightforward. The general solution is rather complex but can be considerably simplified in our case since we have definite values of k_1, k_2, and k_r to substitute in. Eqs. 3.4-18 retain the minimum degree of complexity consistent with condition that the sum of the probabilities that the radical exists as 3, as 4, or as 9 is identically unity at all times. The next higher level of approximation replaces k_1 in the two exponential terms by the sum $k_1 + k_2 + k_r$.

$$\begin{aligned}
(3) &= \left(\frac{k_1+k_r}{k_1+k_2+k_r}\right)\exp(-k_1 t) + \left(\frac{k_2}{k_1+k_2+k_r}\right)\exp\left(-\frac{k_r k_2}{k_1}\,t\right) \\
(4) &= -\left(\frac{k_1}{k_1+k_2+k_r}\right)\exp(-k_1 t) + \left(\frac{k_1}{k_1+k_2+k_r}\right)\exp\left(-\frac{k_r k_2}{k_1}\,t\right) \qquad (3.4\text{-}18) \\
(9) &= -\left(\frac{k_r}{k_1+k_2+k_r}\right)\exp(-k_1 t) - \left(\frac{k_1+k_2}{k_1+k_2+k_r}\right)\exp\left(-\frac{k_r k_2}{k_1}\,t\right) + 1
\end{aligned}$$

The reader can readily confirm that we start out with (3) = 1 and that at long times we have (9) = 1. Predictions for intermediate times are displayed in Table 20 for reaction temperatures of 100, 0, -100, and -150°.

We see from the table that at 100° equilibration of 3 and 4 is underway by 10^{-9} sec and is nearly complete by 10^{-8} sec. The same points are reached at 0° at times which are about a factor of ten longer. We noted in subsection 5C to Section One that yields of analogous cage products are virtually identical for decomposition of ring-opened perester 1 and for that of saturated perester 8 at ~150°. As the hydrocarbon radical from the latter does not have available a reaction step comparable to the rearrangement of 3 to 4, this broadly implies (assuming that our estimate of k_1 is realistic) that at 100° essentially

Table 20. Relative Probabilities at Several Reaction Temperatures that a Radical Species which is Ring-opened at Time Zero will be Ring-opened (3), Ring-closed (4), or Ring-cyclized (9) at Subsequent Times, as Calculated from Eqs. 3.4-18.

Temp., °C	Radical Species	Time From Formation of 3, sec						
		10^{-9}	10^{-8}	10^{-6}	10^{-4}	10^{-1}	10^{6}	10^{13}
100	3	0.739	0.049	0.001	6×10^{-4}	---	---	---
	4	0.256	0.934	0.976	0.545	---	---	---
	9	0.005	0.017	0.023	0.455	1.000	1.000	1.000
0	3	0.964	0.696	2×10^{-5}	2×10^{-5}	1×10^{-5}	---	---
	4	0.035	0.302	0.994	0.944	0.615	---	---
	9	2×10^{-4}	0.002	0.006	0.006	0.385	1.000	1.000
-100	3	1.000	0.996	0.688	6×10^{-9}	6×10^{-9}	2×10^{-9}	---
	4	4×10^{-4}	0.004	0.312	0.999	0.999	0.344	---
	9	10^{-7}	10^{-6}	10^{-4}	5×10^{-4}	5×10^{-4}	0.656	1.000
-150	3	1.000	1.000	0.998	0.791	6×10^{-13}	6×10^{-13}	3×10^{-13}
	4	2×10^{-6}	2×10^{-5}	0.002	0.209	1.000	1.000	0.640
	9	---	---	7×10^{-8}	7×10^{-6}	3×10^{-5}	3×10^{-5}	0.360

all of the cage product is formed in each case within 10^{-9} sec after the perester fragmentation. Interestingly, Noyes has estimated that the rates of diffusive separation of one-contiguous particles will usually allow about 10^{-9} sec for cage reaction to be effected in ordinary solvents (such as cyclohexane, benzene, etc.) (24).

One interesting feature of the kinetic scheme is that the time required for equilibration of 3 and 4 is independent of whether the radical species is initially ring-opened or ring-closed.* This may at first seem paradoxical, since the rate of conversion of 3 to 4 is much larger than that of 4 to 3, but the compensating factor is that a much smaller degree of conversion to the alternative form is required if the radical is initially ring-closed 4.

Following the attainment of equilibrium between 3 and 4, the radical continues to be most probably ring-closed until about 10^{-4} sec at 100° and 10^{-1} sec at 0°, whence ring cyclization through the small equilibrium concentration of 3 becomes important. At -100 and -150°, the corresponding times are predicted to be about 10 days and 300,000 years. This suggests that it should be possible to directly observe the 'classical ring-closed radical' by esr spectroscopy at low temperatures and perhaps even to conveniently measure the rate of conversion to 9 (which is essentially determined by k_2k_r/k_1). In contrast, the much more rapid equilibration of 3 and 4 would be difficult to monitor with

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*Specifically, one finds that equal times are required to form any given fraction of the equilibrium concentration of the second radical species whether the first is 3 or 4.

currently available esr equipment even if a temperature of -150° could be employed.

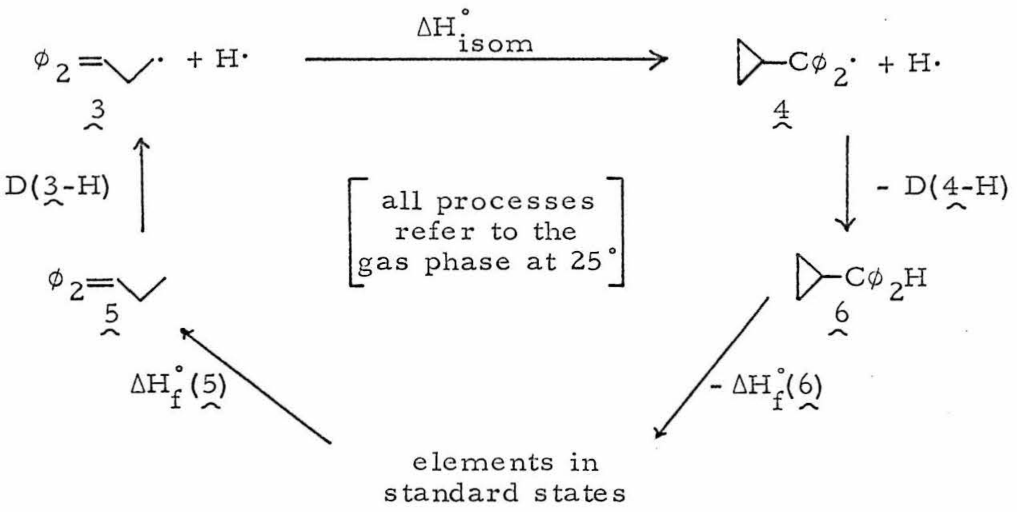
Note that a small probability of being in the ring-cyclized form accumulates on the time scale of the equilibration between 3 and 4; this results from direct competition between ring-cyclization to 9 and rearrangement to 4 while the probability of being in the ring-opened form is still high. Any 'extra' amount of ring-opened hydrocarbon which might be formed in competition with the two processes would similarly be 'early' product. Such material is not accounted for under the mechanistic assumptions of Section Two. As indicated by the probability figures at 0 and 100°, the extent of this early ring-cyclization increases at higher temperatures. However, the conversion to 9 during the radical equilibration is predicted to be only 2.6% at 150°, the highest temperature employed, so the partial failure of the equilibrium assumption is not serious. In any case, there would be no direct effect on the ratio of ring-opened hydrocarbon 5 to dihydronaphthalene 10 treated in Section Two, since the same partitioning factor, $k_a(ZH)/k_r$, would apply at all times. The failure of the assumption would mainly effect the ratio of ring-closed hydrocarbon 6 to ring-opened hydrocarbon 5, as more 5 but less 6 would be formed than we would have predicted. Using eqs. 3.4-1 and 3.4-2 we find that this product ratio would be overestimated by a maximum of about 3% for reaction in neat 1,4-cyclohexadiene at 150°. This is a small factor compared to the experimental uncertaintity in the ratio of 6 to 5 of perhaps 10% under such conditions.

In summary, then, at 100° the cage process are largely completed within 10^{-9} sec of the fragmentation of a molecule of ring-opened perester 1, equilibration of the ring-opened and ring-closed radicals is nearly completed by 10^{-8} sec, and the major portion of ring cyclization and hydrogen abstraction occurs in the neighborhood of 10^{-4} sec. At 0°, comparable figures for the attainment of equilibrium between 3 and 4 and for ring-cyclization are 10^{-7} and 10^{-1} sec.

5. Estimation of Relative Enthalpies of Phenyl- and Methyl-substituted Allylcarbinyl and Cyclopropylcarbinyl Radicals

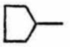
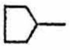
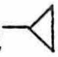
The principal purpose of this subsection is to show that the experimentally inferred difference of -8 ± 3 kcal/mole in the enthalpies of ring-closed radical 4 and ring-opened radical 3 (heading K, p. 277; subsection 2, Section Three) is not inconsistent with chemical and thermodynamic experience. In addition, we shall briefly investigate the manner in which methyl and phenyl substitution may be expected to influence the relative stabilities of so-called ring-opened allylcarbinyl- and ring-closed cyclopropylcarbinyl free radicals.

The thermodynamic cycle diagrammed below shows that the difference in enthalpy of the radicals 3 and 4 may be obtained as the difference of the dissociation energies of the relevant carbon-hydrogen bonds in 5 and 6 less the difference in the enthalpies of the isomeric hydrocarbons. Our approach will be first to estimate the heats of formation of the hydrocarbons. These quantities will then be combined with the estimate $\Delta H^{o}_{isom} = -8 \pm 3$ kcal/mole to infer a value for the difference in the C–H bond dissociation energies. Finally, we shall consider whether that difference is reasonable.



We can estimate $\Delta H^\circ_f(5)$ by correcting the observed ΔH°_f of 58 kcal/mole for 1, 1-diphenylethylene (Table 21) for the effect of substitution of an ethyl group for a vinylic hydrogen. Such an approach is sound, although it will probably seem questionable to readers who have not had the occasion to observe the impressive regularities which heats of formation display as a function of molecular structure, particularly for homologous series. We have indicated in Table 21 two comparisons of the type required here. The first shows that the heat of formation of ethylene decreases by 12. 2 kcal/mole upon substitution of ethyl for hydrogen to give 1-butene. The second comparison, perhaps more appropriate as a model for relating 1, 1-diphenylethylene and 1, 1-diphenyl-1-butene, concerns 2-methylpropene ('1, 1-dimethylethylene') and 2-methyl-2-pentene: the heat of formation of the latter is 11. 6 kcal/mole less than that of the former. Many similar comparisons

Table 21. Literature Values for Heats of Formation (kcal/mole) of Some Hydrocarbons in the Gas Phase at 25°

Compounds	ΔH_f^o	$\delta\Delta H_f^o$	Ref
$CH_2=CH_2$	12.50	12.2	123
$CH_2=CH_2CH_2CH_3$	0.28		123
$(CH_3)_2C=CH_2$	- 3.34	11.6	123
$(CH_3)_2C=CH_2CH_2CH_3$	-14.96		123
$(C_6H_5)_2C=CH_2$	58[a]		128
CH_4	-17.89		123
$C_6H_5CH_3$	11.95	55	123
$(C_6H_5)_2CH_2$	37[b]	52	130
$(C_6H_5)_3CH$	64[c]	53[d]	133
$(C_6H_5)_4C$	90[d]		134
$-CH_2CH_3$	1.7[e]		124
 CH_3	-25.50	4.87	123
 CH_2CH_3	-30.37		123
$(CH_3)_2CHCH_3$	-32.15	4.77	123
$(CH_3)_2CHCH_2CH_3$	-36.92	5.57	123
$(CH_3)_2CHCH(CH_3)_2$	-42.49		123
cyclopropane	12.73		123
$(C_6H_5)CH_2CH_3$	7.12		123
$CH_3CH_2CH_3$	-24.82	26.5	123
CH_3CH_2-	1.7		124
$(C_6H_5)CH=CH_2$	35.22		123

Footnotes for Table 21

[a] From $\Delta H_c^{298}(1)$ = 7393.0 ± 0.6 abs kjoules/mole = 1767.0 ± 0.2 kcal/mole (128a). Translation to ΔH_f^o = 40.4 kcal/mole made using standard heats of formation: ΔH_f^o $CO_2(g)$ = 94.052 kcal/mole; ΔH_f^o $H_2O(1)$ = 68.317 kcal/mole (129). Correction to gas phase made using ΔH_v = 17.5 kcal/mole at 25° (128b).

[b] Based on $\Delta H_f^{298}(1)$ = 21.2 kcal/mole (130a). Correction to gas phase accomplished in two steps using ΔH_{fusion} = 4.2 kcal/mole (130b) and $\Delta H_{sublimation}$ = 19.7 kcal/mole (130c). These values give ΔH_{vap} = 15.5 kcal/mole; a direct determination giving 12.7 kcal/mole is available (131), but was not used as it seems too small in comparison to values of 17.5 kcal/mole for 1, 1-diphenylethylene (128b) and 17 for 1, 1-diphenylethane (132).

[c] This result is based on two determinations of $\Delta H_c(s)$ (2372.2 and 2374.2 kcal/mole) quoted by Cottrell (133). The average gives $\Delta H_f^{298}(s)$ = 39.7 kcal/mole using heats of formation of combusion products quoted in footnote a. Corrected to gas phase using $\Delta H_{sublimation}$ = 23.9 kcal/mole (130c).

[d] Value very approximate; based on an average $\Delta H_c^{298}(s)$ of 3097 kcal/mole from two sources which differed by 11 kcal/mole (134a, 134b). Corrected to a heat of formation using heats of formation of combustion products as in footnote a. The value quoted was then obtained using a heat of sublimation of 28 kcal/mole estimated with reference to values of 19.7 kcal/mole for diphenylmethane and 23.9 kcal/mole for triphenylmethane (130c).

[f] See text.

which may be made from standard compilations of heats of formation (113, 123) such as may be found in the "Handbook of Chemistry and Physics" (113) yield closely similar 'correction factors'.

Thus we obtain $\Delta H_f^o(\underset{\sim}{5})$ as 58 - 12 = 46 kcal/mole. This estimate is probably reliable to ± 2 kcal/mole.

We shall next make use of the orderly variation of ΔH_f^o for successive substitution on methane of phenyl for hydrogen to obtain $\Delta H_f^o(\underset{\sim}{6})$ from ΔH_f^o for methylcyclopropane. It may be seen from Table 21 that disubstitution on methane itself increases ΔH_f^o by 55 kcal/mole, whereas disubstitution on toluene leads to an increase of 52 kcal/mole and disubstitution on diphenylmethane increases ΔH_f by ~53 kcal/mole.*

Unfortunately, no one seems to have anticipated our need for the heat of formation of methylcyclopropane. However, ethylcyclopropane has been studied by Fierens and Nasielski (124). Their heat of combustion at 25°, 808.8 kcal/mole, implies a heat of formation of liquid ethylcyclopropane of -3.1 kcal/mole. The latent heat of vaporization needed to correct this quantity to the gas phase seems to be unavailable, but that of pentane, 4.9 kcal/mole at 25° (125), should be close enough since these C_5 hydrocarbons differ in boiling point at 760 mmhg by only 0.3° (126, 127). This gives $\Delta H_f^o = 1.7$ kcal/mole for ethylcyclopropane.

We can estimate ΔH_f for methylcyclopropane from that for ethylcyclopropane with reference to model processes wherein the role of

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*This last comparison is considerably less reliable than the others; see footnote d to Table 21.

the cyclopropyl group is taken by the isopropyl and cyclopentyl groups (see Table 21). For the latter we find ΔH_f^o (methylcyclopentane) = ΔH_f^o (ethylcyclopentane) + 4.87 kcal/mole. The analogous comparison for isopropyl gives a correction quantity of + 4.77 kcal/mole. Therefore we estimate ΔH_f^o = 6.5 kcal/mole for methylcyclopropane.

Finally, we estimate $\Delta H_f(\mathbf{6})$ = 60 ± 3 kcal/mole by adding +53 kcal/mole to ΔH_f^o for methylcyclopropane for substitution of two phenyl groups.

Thus we have that **6** is less stable than **5** by ~ 14 kcal/mole. Together with the observed $\Delta H_f^o(\mathbf{4}) - \Delta H_f^o(\mathbf{3})$ = -8 ± 3 kcal/mole in cyclohexane--1,4-cyclohexadiene mixtures, this would require D(**3**-H) - D(**4**-H) = 22 kcal/mole with an uncertainty of perhaps ± 6 kcal/mole, assuming that transfer of the equilibrium between **3** and **4** to the gas phase does not greatly effect the difference in enthalpy of the two radicals.[*] We have consistently assumed interaction of the radical center in **3** with the double bond to be negligible and now take D(**3**-H) to be ~98 kcal/mole, this being the observed value for D(C_2H_5-H) (95).

Thus, our estimate for the difference in enthalpy of the ring-closed and ring-opened radicals implies D(**4**-H) = 76 ± 7 kcal/mole.

Although quantitative data on dibenzylic C–H bond dissociation energies are lacking,[**] we believe this estimate would be reasonable

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[*] The effect of the transfer would probably be to make the enthalpy difference smaller than in the gas phase by preferential solvation of the less stable ring-opened radical. This might well lower the mean D(**4**-H) given below by one or two kcal/mole.

[**] D($(C_6H_5)_2$CH–H) = 72 kcal/mole has often been quoted (51, 135). However, no mention of this determination is made in recently

even if the cumulative uncertainty were only ± 3 kcal/mole. In support of this assertion we can cite D($C_6H_5CH_2$-H) = 85 kcal/mole with confidence (95 , 135) and can make a reasonable case for D((C_6H_5)$_3$C–H = 75 kcal/mole (51 ,135). The latter value may be obtained as $\frac{1}{2}$(11 + 35 + 104) from a thermochemical cycle employing the heat of hydrogenation of dissolved hexaphenylethane in ethyl acetate (- 35 kcal/mole (138)) and the heat of dissociation of hexaphenylethane in solution (11 ± 1 kcal/mole, insensitive to solvent (139)) in conjunction with the heat of dissociation of molecular hydrogen in the gas phase. As D(CH_3-H) is 104 kcal/mole (95), we see that the first substitution of phenyl for hydrogen lowers D(R-H) by 19 kcal/mole. Substitution of a second phenyl group may be expected to effect a smaller decrease (a) because of inhibition of resonance through rotation of the phenyl rings in diphenylmethyl to noncoplanar conformations as the result of repulsive interactions of *ortho*-hydrogens (140) and (b) by virtue of the commonly observed phenomenon of saturation upon successive substitution.* Thus, D()C_6H_5)$_2$CH–H) = 75 kcal/mole would seem to be a reasonable guess, and D(**4**-H) should not be greatly different; the extra stabilization which would probably be expected for substitution of cyclopropyl for hydrogen in the presence of two phenyl groups in a hypothetical

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advanced bond dissociation energy compilations (95 ,136 , 137). Apparently those closest to the field have judged the determination to be invalid, along with a number of others which concern benzylic C–H and C–C bonds.

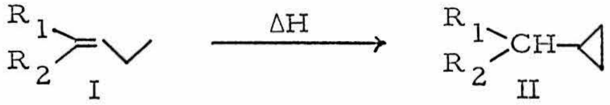
*For example, successive substitution of methyl for hydrogen gives the series D(CH_3-H) - 104, D(C_2H_5-H) = 98. 0, D((CH_3)$_2$CH-H) = 94. 5, D((CH_3)$_3$C-H) = 91 (95).

strain-free system could well be of lesser magnitude than the destabilization of the real system due to an increase in the out-of-plane rotation of the phenyl rings. A similar compensation phenomenon may account for $D((C_6H_5)_3C\text{-}H) \cong 75$ kcal/mole.

We have recorded our estimates of the heats of interconversion of differently substituted allylcarbinyl-cyclopropylcarbinyl free radicals in Table 22. Much of the requisite information on the heats of formation of the isomeric hydrocarbons has been considered in passing above. We require here three additional estimations. The heat of formation of isopropylcyclopropane can be obtained as $1.7 - 5.6 = -3.9$ kcal/mole by correcting that for ethylcyclopropane for substitution of methyl for hydrogen. Table 21 shows that this substitution requires a correction factor of 5.6 kcal/mole where the role of the constant cyclopropyl group is taken by isopropyl. To estimate ΔH_f^o for benzylcyclopropane, we start with $\Delta H_f^o = 7.1$ kcal/mole for ethylbenzene. The hypothetical process here will be to substitute cyclopropyl for methyl. The result is an increase in the heat of formation of 26.5 kcal/mole where the constant group is ethyl rather than our tolyl. We estimate thereby ΔH_f^o(benzylcyclopropane) = 34 kcal/mole. Finally, we estimate ΔH_f^o(<u>trans</u>-1-phenyl-1-butene) as 23 kcal/mole by applying the same 12 kcal/mole correction to ΔH_f^o(styrene) as was done earlier to get $\Delta H_f^o(\underset{\frown}{5})$ from that for 1,1-diphenylethylene.

As shown in the upper region of Table 22, these estimations predict a smooth enhancement of the heat of interconversion of the isomeric hydrocarbons with successive substitution of phenyl or methyl for hydrogen. The trend is undoubtedly due mainly to stabilization of

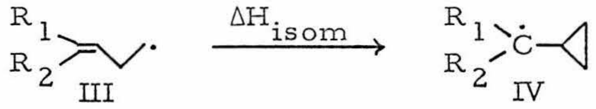
Table 22. Estimated Enthalpies of Interconversion of Some Isomeric Allylcarbinyl and Cyclopropylcarbinyl Hydrocarbons and Free Radicals.



R_1	R_2	$\Delta H_f^o(II)$[c]	$\Delta H_f^o(I)$[c]	$\Delta H \equiv$ $\Delta H_f^o(II) - \Delta H_f^o(I)$
H	H	6.5[a]	0.28[b]	6
CH_3	H	1.7[b]	- 7.59[b]	9
CH_3	CH_3	-3.9[a]	-14.96[b]	11
C_6H_5	H	34[a]	23[a]	11
C_6H_5	C_6H_5	60[a]	46[a]	14

[a] Estimated; see text. [b] From Table 21.

[c] kcal/mole; for the gas phase at 25°.



R_1	R_2	$\Delta H_{isom}^{d,e}$	D(IV-H)[e,f]	D(III-H)[e,f]
H	H	+ 3	95	98
CH_3	H	+ 3	92	98
CH_3	CH_3	+ 2	89	98
C_6H_5	H	- 5	82	98
C_6H_5	C_6H_5	-8 ± 3[g]	76[h]	98

[d] Obtained as $\Delta H_f^o(II) - \Delta H_f^o(I) + D(IV\text{-}H) - D(III\text{-}H)$.

[e] kcal/mole; for the gas phase at 25°. [f] Estimated; see text.

[g] Observed value in hydrocarbon solution; see text.

[h] Adopted to fit observed value for ΔH_{isom}; see footnote g.

the double bond in the allylcarbinyl isomer.

Estimates of the C–H bond dissociation energies in the isomeric hydrocarbons, when combined with the relative enthalpies of the hydrocarbons, give the predicted heats of isomerization of the allylcarbinyl-type radical to the cyclopropylcarbinyl form. We have assigned D(C–H) = 98 kcal/mole for all the ring-opened hydrocarbons with reference to D(ethyl-H) = 98.0 (95). The assignments for the cyclopropylcarbinyl structures are intended to broadly reflect the greater kinetic reactivity of methyl hydrogen in methylcyclopropane as compared with a 'typical' primary hydrogen of isopentane. Observed enhancement factors (on a per-hydrogen basis) are about 3 for competitive hydrogen abstraction by t-butoxy radicals at 68° and 5.5 at 0° (118a), about 16 for competitive abstraction by atomic chlorine at 0° (118a) and 6.1 for hydrogen abstraction by the polystyryl radical 79°, determined by comparison of chain-transfer constants (118b). Unfortunately, these data can not be simply translated into differences in bond-dissociation energies. However, some lowering upon substitution of cyclopropyl for methyl on ethane is evidently indicated, and we have employed D(cyclopropylcarbinyl-H) = 95 kcal/mole. We have similarly estimated D(methylcyclopropylcarbinyl-H) = 92 kcal/mole with reference to D(isopropyl-H) = 94.5 kcal/mole, and D(dimethylcyclopropylcarbinyl-H) = 89 kcal/mole with reference to D(t-butyl-H) = 91 kcal/mole (95). It seems reasonable that the extra stabilization for α-cyclopropyl over α-methyl will be diminished by successive substitution of methyl groups for hydrogen at the prospective radical center. Finally, we have assigned D(phenylcyclopropylcarbinyl-H) = 82 kcal/mole with reference to D(benzyl-H) = 85 (95).

The calculated enthalpies of isomerization of the isomeric radicals shown in Table 22 atfirst surprised us; we had expected that substitution of methyl and then phenyl groups onto the parent four-carbon system would smoothly lower the enthalpy of interconversion to the strongly negative figure of -8 kcal/mole observed for the diphenyl-substituted system. It appears that this is not the case--that substitution of methyl nearly equally stabilizes the ring-opened hydrocarbon (hence the ring-opened radical) and the ring-closed radical. Substitution of phenyl for hydrogen is required for the latter factor to become dominant.

We noted in the OVERVIEW that interest came to be focused on the diphenyl-substituted system because the analogous unsubstituted and dimethyl-substituted systems gave, with but one exception, only traces of the ring-closed hydrocarbon as product (pp. 9-10). The motivation for employing methyl and phenyl substituents was to effect closer competition in product formation in order to make the system experimentally tractable. Indeed, Howden found that the diphenyl-substituted system gave ring-closed hydrocarbon 6 and ring-opened hydrocarbon 5 in the proportions of about 20:1 upon decomposition of ring-opened perester 1 in the presence of the powerful hydrogen donor, tri-*n*-butyltin hydride (Table 12).

Estimated enthalpies quoted in Table 22 clearly show that the price of effecting close competition in the formation of products is the creation of an enormous difference in reactivity of the isomeric radicals 3 and 4, as reflected in the strengths of the carbon-hydrogen bonds they may form, offset by a large difference in the stability of the radicals. The natural result, as we have seen in subsection 2, is that hydrogen donors of differing reactivity respect to greater or lesser degrees the intrinsic difference in reactivity of the radicals and so give rise to widely varying ratios of ring-opened and ring-closed products.

The large difference in stability of the isomeric radicals **3** and **4** almost certainly has the additional effect of overriding any driving force for radical stabilization via σ-electron delocalization which may have existed in the parent four-carbon system, where both the allylcarbinyl radical and the cyclopropyl-radical are essentially primary radicals. The apparent failure to observe a nonclassical radical in the system investigated here does not now seem very surprising.

It therefore remains for future researchers to demonstrate the existence of nonclassical free-radical intermediates or to present data which *would* support a general presumption against σ-electron delocalization.

EXPERIMENTAL SECTION

Melting points and boiling points are uncorrected. The melting points were taken on a Büchi apparatus.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Infrared spectra were determined using either a Beckman infrared spectrophotometer, Model IR-7, or a Perkin-Elmer Infracord, Model 237.

Nuclear magnetic resonance spectra were routinely recorded with Varian Associates A-60 or A-60A spectrometers. In special cases, a Varian Associates A-56/60A spectrophotometer equipped with a Varian C-1024 Time Averaging Computer was employed.

Gas chromatographic analyses were carried out on a Perkin-Elmer Model 800 gas chromatograph fitted with a flame-ionization detector and a Perkin-Elmer Model 194 printing integrator. The column routinely employed was 6-12 ft of aluminum tubing (1/8 in o.d.) packed with 10% Ucon polar 50 HB 5100 on 80-100 mesh HMDS treated Chromasorb W. Also employed were columns of silicone oil (SE-30) and Apiezon L on the same stationary phase.

1. Solvents (Hydrogen Donors)

Cyclohexane, benzene, and methanol were Matheson Coleman & Bell Chemicals, Spectroscopic Grade, used as received.

Cumene was purified by the method of Vogel (141) before use.

Indene was distilled at atmospheric pressure from sodium and then again under reduced pressure at ~35° through a Vigreaux column. Material from a center fraction was sealed under nitrogen and stored at 0° until use.

n-Octane [Phillips Petroleum Company Pure Grade (99 Mol% Minimum)] was stirred over concentrated sulfuric acid until fresh portions of the acid were only weakly colorized. The hydrocarbon was then washed twice with 10% sodium carbonate solution, dried over magnesium sulfate, and finally distilled from sodium, bp 124.0 - 124.5° at atmospheric pressure.

1,4-Cyclohexadiene was obtained from Columbia Organic Chemicals Co., Inc. and from Aldrich Chemical Co., Inc. The Columbia material was used in experiments reported in Tables 1 and 3. Analysis by vpc on Ucon polar indicated a purity of 99.9%, with impurities of benzene(?), 0.1%, and 1,3-cyclohexadiene(?), 0.02%. Experiments reported in Tables 2, 4, 5, and 6 employed Aldrich preparations, subsequently observed to contain 0.01 -- 0.1% 1,3-cyclohexadiene and to develop an impurity upon heating at approximately the retention time of one of the reaction products from the perester decompositions (142). No purification was undertaken with the exception of distillation at atmospheric pressure through a small Vigreaux column immediately before use.

Triethyltin hydride was prepared from triethyltin bromide (Orgmet, Inc.) by reduction with lithium aluminum hydride. In a typical preparation, 58 g (0.202 mole) triethyltin bromide in 250 ml diethyl ether (Mallinckrodt Anhydrous Ether, Analytical Reagent) was added slowly to 7.7 g (0.20 mole) lithium aluminum hydride in 300 ml diethyl ether. No exothermicity was noted. The reaction mixture was stirred for 4 hr at reflux, after which 28 ml of a 4.45% aqueous sodium hydroxide solution was cautiously added after the reaction flask had been swept with nitrogen. The reaction mixture was then filtered with suction and distilled through a Vigreaux column until the pot temperature reached 65° to remove most of the diethyl ether. The residual material was fractionated through the same column at about 25 mm. A center fraction distilled at 52-53°; 26.5 g (63%). The identity of the product was conclusively established by comparison of an infrared spectrum with that reported in the literature (143).

The triethyltin hydride was either used immediately or was degassed and sealed into specially prepared two-chambered glass vessels at $\sim 10^{-3}$ mm (three freeze-pump-thaw cycles using liquid nitrogen). It was generally possible to transfer the triethyltin hydride from the one chamber to the other immediately before use in the perester decompositions by cooling the recepticle in liquid nitrogen while warming the side with the tin hydride in tepid water. This could usually be done some days, weeks, or occasionally months after the original sealing, but sufficient hydrogen pressure built up in some tubes that the tin hydride would not distill. The main decomposition product appears to be hexaethylditin; in one case, such material was treated with bromine in diethyl ether and the resultant triethyltin bromide was reconverted to triethyltin hydride as above.

Diethyl ether and tetrahydrofuran were refluxed over sodium -- benzophenone (144) for several days and were distilled from the same pot immediately before use.

Tetraethyltin was used as obtained from Orgmet, Inc.

2. Starting Materials and Reaction Products

(γ,γ-Diphenylallyl)acetic Acid. - (γ,γ-Diphenylallyl)carbinyl bromide [43 g, 0.15 mole, prepared by treatment of diphenylcyclopropylcarbinol (Aldrich Chemical Co., Inc.) with phosphorus tribromide as described by Howden (145)] in 400 ml anhydrous ether was added with stirring to 4.0 g (0.165 mole) magnesium shavings in a nitrogen atmosphere over the course of 1 hr. After an additional hour at reflux, the reaction mixture was cooled in a Dry Ice-acetone bath and *ca.* 20 g finely powdered Dry Ice (about a two-fold excess) were added. After a few minutes at -80°, the bath was removed and the reaction mixture allowed to warm up. At -60° a second portion of 20 g Dry Ice was added. When the reaction mixture had reached -10°, it was poured into 400 ml ice-cold half conc. hydrochloric acid in a separatory funnel. The funnel was shaken and the aqueous layer separated and shaken with 200 ml ether. The combined ether solutions were extracted with two 150-ml quantities of a solution of 20 g (0.5 mole) sodium hydroxide in 300 ml water. The aqueous extracts were acidified with concentrated hydrochloric acid, upon which the white acid crystallized. The solid was collected by filtration, washed liberally with water, and air-dried. The product was crystallized from hexane and gave a first crop, 27.1 g, mp 82.8 -83.5°, and a second crop, 3.0 g, mp 81-82° (total 80%); lit. (146) mp 83-83.5°.

***t*-Butyl (γ,γ-Diphenyallyl)peracetate.** - An initial sample, used for runs displayed in Table 1 and for many of those in Table 8, was material left by Howden. Later samples were prepared by a modification of Howden's procedure (147). In one such preparation, 5 g (20 mmoles) of γ,γ-diphenylallylacetic acid was refluxed for 3 hr with 1.77 ml freshly distilled thionyl chloride in 50 ml spec. grade benzene. The solvent and excess thionyl chloride was then removed on the rotatory evaporator at a bath temperature of 35-40°, after which 50 ml fresh benzene was added to the residue and stripped as before. The crude acid chloride in 50 ml pentane was then added over the course of 0.5 hr to 4 ml *t*-butyl hydroxide (usually Lucidol *t*-butyl hydroperoxide - 90, *ca.* 40 mmoles, 100% excess) and 1.74 ml pyridine (22 mmoles) in 200 ml pentane cooled in an ice-salt bath and stirred magnetically. After an additional 2 hr at about 0°, the pentane solution (from which pyridine hydrochloride had precipitated) was washed with water, with two 150-ml portions of 10% sulfuric acid, and finally with two 150-ml portions of 10% aqueous sodium bicarbonate. The organic layer was then dried over magnesium sulfate and passed through a column of 5 g Florisil, followed by 60 ml pentane. The eluent was then evaporated, affording 5.25 g of slightly yellow oil which solidified on addition of a crystal of authentic perester. The crude perester was crystallized from pentane to give a first crop of 4.0 g, mp 40.5-42°; lit. (147) mp 42-42.5°. A second crop, 0.5 g, had mp 41-42.5°; total, 4.5 g (72%).

***t*-Butyl 5,5-diphenylperpentanoate** was material prepared by Howden (148), crystallized from pentane to mp 50-50.5° before use.

Diphenylcyclopropylacetic acid initially kindly supplied by Dr. Adelbert Maercker, was subsequently prepared by carbonation of diphenylcyclopropylcarbinylpotassium as described by Maercker and Roberts (69).

Diphenylcyclopropylacetyl Chloride. - A solution of 8.7 g diphenylcyclopropylacetic acid (3.44 mmoles) in 11 ml thionyl chloride (15 mmoles) and 10 ml benzene was refluxed for a 3 hr period after which the benzene and excess thionyl chloride were removed on the rotatory evaporator (bath temp. ca. 40°). Benzene (ca. 25 ml) was added and similarly stripped, then ca. 25 ml diethyl ether was added and stripped. The residual yellow oil, which solidified on scratching, gave 6.73 g of light yellow crystals upon sublimation. This material was resublimed; 4.9 g of colorless crystals, mp 66-68° (52%).

Crystallization from n-hexane followed by 'sublimation' at 65-70° (0.3 mm)(the material was liquid for most of the procedure) afforded an analytical sample, mp 68-69°.

Anal. Calcd. for $C_{17}H_{15}ClO$: C, 75.41; H, 5.58; Cl, 13.10. Found: C, 75.05; H, 5.73, Cl, 12.93.

The nmr spectrum of a sample in carbon tetrachloride was as expected and appeared to be unchanged after heating at 88° for 13 hr. Integration following the period of heating indicated, with respect to 10 aromatic protons, 0.9 (tertiary cyclopropyl) protons (multiplet, 2.1-2.6δ), 2.0 (secondary cyclopropyl) protons (multiplet, 0.5-1.1δ), and 1.9 (secondary cyclopropyl) protons (multiplet, 0.0-0.5δ). Separation of the secondary cyclopropyl protons into two groups of resonances was also observed for the precursor acid and for the derived *t*-butyl perester (see below). No trace of vinylic protons (which would indicate ring-opened products) could be found. The carbonyl band of a sample in carbon tetrachloride was found at 1785 cm^{-1}.

Sodium *t*-butyl peroxide was prepared essentially as described by Lorand and Bartlett (27) by treatment of sodium hydride (Metal Hydrides, Inc., 55% suspension in mineral oil, 15.9 g, 0.36 mole) with *t*-butyl (Lucidol, passed through a column of molecular sieves and distilled under reduced pressure, 27.6 g, *ca.* 15% excess) in diethyl ether (1.5 l., freshly distilled from lithium aluminum hydride). The crude product, collected by suction filtration and washed with fresh ether, weighed 36.5 g when dry (114% based on the assay of 55% for the sodium hydride suspension claimed by the manufacturer). Titration with standard hydrochloric acid indicated a neutralization equivalent of 111 (theoretical, 112), compared to 131 for the preparation described by Lorand and Bartlett. The product was ground in a morter and partitioned into several vials which were then sealed with wax and maintained at 0° until use in the conversion of diphenylchclopropylacetyl chloride to *t*-butyl diphenylcyclopropylperacetate.

Declining success of perester preparations with the age of the sodium *t*-butyl peroxide suggests that the material not be used if more than a few months old when stored in the powdered state [Lorand and Bartlett suggest that the material is stable for longer periods if stored in cake form; they also suggest that only freshly prepared material be ground (27)].

t-Butyl Diphenylcyclopropylperacetate. - To 1.07 g (3.95 mmoles) diphenylcyclopropylacetyl chloride in 75 ml pentane at -10° was added 0.87 g (100% excess) powdered sodium t-butyl peroxide. The reaction mixture was maintained between -10 and 0° for two hr with magnetic stirring. A sample withdrawn after 1.5 hr displayed a band in the infrared at 1765 cm^{-1} in place of the carbonyl absorbance of the acid chloride at 1785 cm^{-1}, indicating that the reaction had gone to completion. The pentane solution was filtered with suction through Celite in fine sintered-glass funnel, followed by 50 ml ice-cold pentane. The solution was concentrated at 0° to about 3 ml on a rotatory evaporator and pipetted into a small vessel with a nitrogen-inlet arm. The flask was washed with 5 ml pentane and the resulting solution was added to that in the small vessel, upon which some white crystals formed. The small vessel was flushed with nitrogen and cooled in several stages to -20°, whence crystallization seemed to be complete. The pentane solution was then withdrawn under positive nitrogen pressure with a syringe. Fresh pentane was added and the crystals were dissolved by warming on a steam bath for a minimal period; 15 ml pentane were required to effect solution. On cooling to -20° and scratching, the crystals reformed. After 0.5 hr at -30° the pentane solution was again removed under positive nitrogen pressure. The solution which adhered to the crystals was largely removed by maintaining the crystals in vacuo for 1 hr at -10 to 0°. The yield was 0.53 g (38%).

A nmr spectrum was obtained at a probe temperature of about -10° on a portion of the above material (perester batch (1), p. 389) in carbon tetrachloride. Integration (2 sweeps each way) indicated, with respect to 10 aromatic protons, 3.8 secondary cyclopropyl protons in broad resonances much like those for the acid chloride and 9.2 methyl(*t*-butyl) protons. There was also a singlet at about 2.1δ corresponding to 0.8 protons; this may arise from water introduced during the prior manipulation of the perester at about 0° in the preparation of the reaction tubes for perester batch (1), as described below (p. 389). No trace of olefinic resonances could be seen.

A sample from another preparation melted with effervescence at about 65° when rapidly heated (perhaps 20 to 30° per min).

Analysis of active oxygen in t-butyl diphenylcyclopropylperactate was undertaken to obtain further evidence that the above preparation does yield the perester and to show that the sensibly constant yield of diphenylcyclopropylmethane of 15% for runs collected in Table 2 is not simply attributable to contamination of the perester by the hydrocarbon. The analytical method employed in the determination of active oxygen is that reported by Silbert and Swern (149).

Two samples of freshly prepared perester were analyzed. The first consisted of 76.4 mg perester plus 11.1 mg diphenylcyclopropylmethane in 25 ml glacial acetic acid containing a trace of ferric chloride. To this was added 2 ml of a nearly saturated sodium iodide solution. The mixture was swirled and allowed to stand in the dark for 15 min in a stoppered flask. Titration of the liberated iodine required 9.90 ml of 0.462 N sodium thiosulfate (standardized against primary standard potassium iodate). Starch solution was added to intensify the end point when the original iodine color had begun to fade. A pair of blank titrations required 0.09 and 0.13 ml of the thiosulfate solution. Using the equation given by Silbert and Swern (149), the above quantities correspond to an active oxygen content for the perester sample of 4.73%. That calculated for $C_{21}H_{24}O_3$ is 4.93%. Therefore, the purity of the perester is 96%.

A second perester sample (77.6 mg) required 9.73 - 0.11 = 9.62 ml of the thiosulfate solution, implying an active oxygen content of 4.58% and a purity of 93%. The average, 94.5%, is quite satisfactory.

To each of the titrated samples was added ca. 100 ml quantities of pentane and of water. Each of the two-phase systems was shaken and the aqueous phase drained off. Extraction of the organic layer with 5% sodium bicarbonate solution allowed the isolation of nonacidic materials. The pentane was evaporated and known quantities of diphenylmethane were added to the two samples. Analysis by vpc showed that the first sample contained 11.1 mg diphenylcyclopropylmethane, the precise amount originally taken, but that the second contained only 0.7 mg of diphenylcyclopropylmethane, or of some material of closely similar retention time. Therefore, little diphenylcyclopropylmethane could have been present in the initial perester samples. Portions of the same perester preparation were subjected to degassed thermal decomposition at 70° in cyclohexane and 1,4-cyclohexadiene. Product compositions inferred by vpc analysis agreed favorably with those reported for analogous runs in Tables 1 and 9.

4,4-Diphenyl-3-buten-1-ol-1,1-d_2 was prepared by the method of Howden (150). From 35 g of γ,γ-diphenylvinylacetic acid (151) was obtained 22.9 g (70%) of the labeled alcohol.

4,4-Diphenyl-1-1,d_2-butene-1-yl *p*-toluenesulfonate was prepared from the above alcohol by a modification of the Tipson procedure for ethyl tosylate (152). The following procedure was found to be satisfactory when using unlabeled materials. To a stirred solution of 22.6 g deuterium-labeled alcohol (10 mmoles) in 50 ml pyridine (dried over and then distilled from barium oxide; stored over sodium hydroxide pellets until use) cooled in an ice-salt bath was added over *ca.* 10 min a solution of 21.0 g tosyl chloride (11 mmoles, freshly crystallized from ligroin) in 38 ml pyridine. The reaction mixture was maintained in the ice-salt bath for an additional 10 min, after which 250 ml of ice-cold 5 N sulfuric acid was added over *ca.* 5 min. The crude off-white tosylate oiled out and then solidified on scratching; it was collected by suction filtration, washed liberally with water, and air-dried. Crystallization at 0° of the crude material (35 g) from *ca.* 400 ml of ether-pentane (about 2:1 by volume) afforded a first crop, 19.7 g, mp 83.5-84.5°; lit. (153) mp 84.5-85.5° for (γ,γ-diphenylallyl)-carbinyl *p*-toluenesulfonate. Concentration of the mother liquor produced a second crop which was recrystallized from ether-pentane; 1.7 g, mp 83-84°. Total, 21.4 g (57%). A nmr spectrum showed that there had been no rearrangement of the deuterium label.

Deuterium-labeled (γ,γ-diphenylallyl)acetonitrile. - The following procedure was found to be satisfactory when using unlabeled materials. The above deuterium-labeled tosylate (21.4 g, 56 mmoles) and 30 g sodium cyanide (0.6 moles) were placed in a 1-l., three-necked, round-bottomed flask fitted with a glass-paddle stirrer and a reflux condenser with a drying tube. Absolute methanol (450 ml) was added and the reaction mixture was warmed to and maintained at reflux for 12 hr. Most of the sodium cyanide dissolved. The reaction mixture was then distilled with stirring under reduced pressure to remove most of the methanol. Water (400 ml) and diethyl ether (400 ml) were then added. The resultant two-phase system was stirred for 20 min and then poured into a separatory funnel. The red-brown aqueous phase was drained off and the etheral layer was washed with 300 ml water, dried (magnesium sulfate), and evaporated. The brown residue (11.5 g) was crystallized from pentane-ether-acetone and then from 60-70° ligroin to give a first crop of 7.2 g, mp 66-67°. A second crop weighed 1.5 g. The total was 8.7 g (65%).

The nitrile was not investigated by nmr, but the acid which resulted from the following preparation was found by nmr to contain 1.4_2 g-atoms of deuterium per molecule. Presumably the deuterium was washed out in the preparation of the nitrile by reversible attack of cyanide anion at the label position to give the α-cyano carbanion.

Deuterium-labeled (γ,γ-Diphenylallyl)acetic Acid. - The following procedure was found to be satisfactory when using unlabeled materials. The above nitrile (8.7 g) was treated with 65 ml of a 1:1:1 mixture by volume of sulfuric acid, glacial acetic acid, and water at reflux for 1.5 hr. When the reaction mixture had cooled to room temperature, it was poured onto *ca.* 600 ml of a mixture of ice and water. The brownish material which solidified was filtered off and taken up in ether. The etheral solution extracted with quantities of 1 N sodium hydroxide until the aqueous layer remained basic. The combined aqueous extracts were then acidified with hydrochloric acid. The product was removed by filtration, washed liberally with water, air-dried, and then crystallized from ligroin; 7.6 g (81%).

A carbon tetrachloride solution of sample recrystallized from hexane was investigated by nmr to determine the extent of deuteration. Ideally, one would also want to confirm the position of the label, but it was not possible to do this by nmr because the spectrum of the unlabeled acid gives only a somewhat broadened doublet (splitting ca. 3.5 Hz) at 2.3 δ for the four methylene protons; and in the α,α-d_2 compound one would expect a doublet spit by ~7 Hz due to interaction with the vinylic proton of the two remaining methylene protons. It was, however, possible to infer from the deuterium distribution in a reaction product from decomposition of the derived t-butyl perester that the deuterium is in the α-position with respect to the carboxyl group (p. 396); i.e., no detectable scrambling of the α- and β-carbons (such as would be expected if formation of the tosylate or its conversion to the nitrile had involved carbonium-ion intermediates) had occurred in the preparation of the acid.

The deuterium content was found to be $1.4_2 \pm 0.09$ g-atoms per molecule by nmr analysis. To obtain this number, the methylene and olefinic absorbance regions were carefully integrated using 5 sweeps upfield and a similar number downfield. A portion of these were carried out on the labeled sample and then a tube containing the unlabeled acid in a closely similar concentration was substituted in the probe for 2 or 3 sweeps. A further number of sweeps was then carried out on the labeled sample, then on the unlabeled sample, and so on until

10 integral traces had been accumulated for each sample. With respect to one vinyl proton in each case, we found 2.55 ± 0.09 methylene protons for the labeled sample and 3.96 ± 0.08 methylene protons for the unlabeled sample. As the latter value should be 4.00, we adjusted the former upward slightly to 2.58 ± 0.09, from which the deuterium content was obtained by difference. Use of the aromatic absorbance as the standard gave an identical mean value. Thus, the extent of deuteration is 71%.

Deuterium-labeled *t*-butyl (γ,γ-diphenylallyl)peracetate was prepared from the above acid in essentially the manner described for the unlabeled material (p. 376). From 3.3 g of the labeled acid we obtained 1.9 g of the perester, mp 41-42° (46%). This material was used in the label-equilibration studies reported below (p. 394 - 399).

Diphenylcyclopropylmethane, 1-phenyl-3,4-dihydronaphthalene, 1-phenyl-1,2,3,4-tetrahydronaphthalene and 1-phenylnaphthalene were samples prepared by Dr. Adelbert Maercker (69).

1,1-Diphenyl-1-butene was prepared by hydrolysis of the Grignard reagent of (γ,γ-diphenylallyl)carbinyl bromide as described by Howden (146).

***t*-Butyl (γ,γ-diphenylallyl)carbinyl ether** was prepared by treatment of the Grignard reagent of (γ,γ-diphenylallyl)carbinyl bromide with *t*-butyl perbenzoate (Ram Chemicals, Inc.) according to the general procedure of Lawesson and Yang for conversion of halides to *t*-butyl ethers (154). From 2.0 g of the bromide was obtained 0.6 g of product by distillation (0.2 mm) of the crude material in a small but thermally inefficient distillation apparatus at a bath temperature of

170-180°. The nmr spectrum of a carbon tetrachloride solution was as expected. Bulb-to-bulb distillation at 0.2 mm and a bath temp of 115-120° afforded an analytical sample which was 98% pure by vpc analysis on Ucon polar (three impurities in about equal amounts, one to somewhat longer retention time).

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.42; H, 8.66.

Diphenylmethylenecyclopropane was prepared by treatment of 3-bromopropyltriphenylphosphonium bromide (from treatment of 1,3-dibromopropane with triphenylphosphine) with 2 equivalents of phenyllithium in the presence of excess benzophenone (155). A preparation of this material in 80% yield was shortly thereafter reported by Sisido and Utimoto who employed the same route but used sodium hydride plus a catalytic amount of ethanol as base. Our material was heavily contaminated with biphenyl (presumably formed in our preparation of phenyllithium from bromobenzene), and inefficient purification via chromatography on alumina followed by sublimation *in vacuo* afforded a 20-mg sample which was pure to vpc (Ucon polar) and had mp 66-67° [lit. (156) mp 64.5-65.5°] (0.5%). The compositions and weights of the discarded chromatography fractions indicated an overall yield of 20%. A mass spectrum obtained at low ionizing voltage displayed a parent peak at m/e 206, as required. The nmr spectrum of a sample in carbon tetrachloride was as reported by Sisido and Utimoti (156) and integrated correctly.

1,4-Diphenylbutane was prepared by hydrogenation of 1,4-diphenyl-1,3-butadiene (Aldrich) using standard procedures (157).

The crude yellow oil which was isolated solidified on scratching. The product was crystallized from pentane and had mp 53-55°; lit. (158) mp 51-52°. The nmr spectrum of a sample in carbon tetrachloride solution was as expected. No olefinic protons could be found.

Triethyltin (γ,γ-Diphenylallyl)acetate. - (γ,γ-Diphenylallyl)-acetic acid (1.0 g, 4.0 mmoles) was placed in a thick-walled glass tube, 1 ml triethyltin hydride (6.1 mmoles) and ca. 5 ml n-octane were added, and the tube was sealed. On warming to effect solution of the carboxylic acid, it appeared that the reaction had begun and that the tin ester had started to crystallize from solution. The tube was heated at 135° for one hour and opened after it had cooled to room temperature. The tin ester was collected by filtration in a sintered glass funnel, through which a few ml of tetrahydrofuran was then passed, upon which the ester, but apparently not tin oxides which had also been formed, dissolved. The clear tetrahydrofuran solution was evaporated and the white residue was taken up in and crystallized from n-hexane; 615 mg (34%), mp 121.5-123°. The relatively low yield probably represents inefficient isolation.

The nmr spectrum of a carbon tetrachloride solution indicated, with respect to 10 aromatic protons, 4.0 methylene protons in a doublet (as in the acid) at 2.4 δ, 14.5 ethyl protons in a broadened singlet at 1.2 δ, and the expected vinylic resonance at 6.0 δ (not accurately integrable because of its low intensity). An infrared spectrum in carbon tetrachloride displayed a carbonyl band at 1651 cm^{-1}.

Crystallization from n-hexane afforded an analytical sample of mp 123-124°.

Anal. Calcd. for $C_{23}H_{30}SnO_2$: C, 60.42; H, 6.61, Sn, 25.96. Found: C, 60.47; H, 6.79; Sn, 25.81.

3. Procedures

Degassed Thermal Decompositions of Peresters. - Product studies reported in Tables 1 through 11 were carried out on small quantities of perester, usually 15-30 mg. Generally, a quantity of perester was weighed into a reaction tube fashioned from 8-mm heavy-walled glass tubing and a measured volume (0.5-2 ml) of the solvent or of a solution of two solvents combined in known weights was added. In some cases, particularly for series of runs investigating variable or low perester concentrations (Tables 4, 5, 6) and for runs in Table 11, stock solutions of perester (in n-octane or benzene for runs in Table 11) were made up and aliquots were transferred by syringe to reaction tubes or were diluted to prepare solutions of low perester concentration.

Runs with t-butyl (γ,γ-diphenylallyl)peracetate or t-butyl 5,5-diphenylperpentanoate employed samples freshly recrystallized from pentane to mp 42-43° and mp 50-50.5°, respectively. t-Butyl diphenylcyclopropylperacetate was always freshly prepared material. It was necessary to maintain the latter perester in a stoppered flask at 0° while not actually manipulating the material. On the one occasion on which the perester was handled at room temperature, after about 5 to 10 minutes at room temperature the perester sample instantaneously liquified and decomposed sufficiently rapidly to blow most of the material out of the container. A qualitative examination by vpc of the droplets left on the walls of the container indicated that the usual hydrocarbon products were not formed. It is quite possible that this behavior is not characteristic of the pure perester, for there was always the possibility of contamination by the precursor acid chloride.

One likely result of repeatedly opening a cold flask is concensation of moisture on the contents. The effect on the product composition observed upon thermal decomposition is not known, but it is possible that traces of water and of diphenylcyclopropylacetyl chloride in some samples may have produced hydrochloric acid in sufficient amounts to catalyse the decomposition of the expected cage combination product, diphenylcyclopropylcarbinyl t-butyl ether (15). We commented previously on the apparent absence of this material in certain runs (p. 78, 79). The following groups of runs were made on common perester preparations: (1) - the runs of Table 2 and those in diethyl ether and cyclohexane at 0.05 M perester in Table 9; (2) - the benzene run at 0.2 M perester and the tetraethyltin run of Table 9, and the runs at 35° in Table 11; (3) - the indene runs in Table 7 and the 'large-scale' decomposition described below wherein diphenylcyclopropylcarbinol was isolated (p. 391); (4) - the runs of Table 6; (5) - the runs at 10° in Table 11. The few other runs reported in the data tables were carried out on separate perester sample.

Reported hydrogen-donor concentrations in all cases and initial perester concentrations for runs in Tables 1, 2, 4, 5, and 6 assume no volume change on mixing and a thermal expansion of 12% per 100°C temperature rise over the room temperature preparation for perester solutions. It was found that 1,4-cyclohexadiene undergoes a volume expansion of 15% when heated in a sealed tube from _ca._ 25 to 152°; this amounts to 12% per 100°, assuming that the expansion is linear in the temperature (159). Literature values per 100° temperature rise, again assuming linearity, are 12.1% for benzene, 12.0% for cyclohexane, and 11.5% for _n_-octane (160).

Reaction tubes were degassed using three freeze-pump-thaw cycles and sealed under vacuum. Two procedures were used. In the first, the degassing was carried out at 0.1 to 0.5 mm using a Dry Ice-acetone mixture as coolant. These runs include those of Tables 1, 2, and 3, rows 1 and 2 of Table 7, all but the bottom row of Table 8, and the runs in cyclohexane and diethyl ether in Table 9. In all other cases, degassing was effected at 10^{-4} to 10^{-3} mm using liquid nitrogen.

The sealed reaction tubes were generally immersed in a bath containing an organic solvent of appropriate boiling point at reflux. A constant temperature bath was employed for runs at 10° in Table 11, and an ice-water bath, for runs at 0° in Tables 2 and 9. The following reaction times are typical: for _t_-butyl diphenylcyclopropylperacetate -- 10 days at 0°, 5 days at 10°, two days at 35°, 12 hr at 70°; for _t_-butyl (γ,γ-diphenylallyl)peracetate -- 100 hr at 99°, 10 hr at 131°, 2 hr at 152°; for _t_-butyl 5,5-diphenylperpentanoate -- 140 hr at 100°, 2 hr at 152°.

The general procedure for vpc analysis of reaction mixtures has been previously reported (p. 45).

Special care was taken in runs employing triethyltin hydride as hydrogen donor to minimize contact with air of perester solutions containing the hydride or the hydride itself. Freshly prepared tin hydride was used in the run at 1.89 M hydride in Table 10. In all other cases, hydride which had been stored *in vacuo* in one chamber of a two-chambered apparatus was freshly distilled to the free chamber, as previously noted (p. 374), immediately before use. For runs reported in Table 11 and at 0.01 M hydride in Table 10, the reactions were thermselves carried out in two-chamber vessels, the tin hydride being placed in one chamber, and distilled to that containing the perester after degassing had been effected. In the other cases, the tin hydride was the last of the ingredients to be placed in the reaction tube and the tube was immediately cooled in Dry Ice-acetone and degassed. In the sets of runs in Table 10 at variable hydride concentrations, the reaction mixtures at the higher hydride concentrations had become quite noticeably cloudy before degassing had been effected. At the end of the reaction period, the major portion of the solvent was distilled to the second chamber by cooling in liquid nitrogen. In the other cases, the freshly opened reaction mixtures were distilled through a short Vigreaux column under aspirator pressure using a bath temperature of 60 to 65° until the volume (initially about 25 ml) had been reduced to 0.5 to 1 ml. A quantity of *n*-octane (*ca.* 25 ml) was now added and the distillation of the solvent was repeated. The concentrated reaction mixtures, essentially hydride-free, were then analyzed by vpc using standard procedures.

Isolation of diphenylcyclopropylcarbinol as a secondary reaction product provided evidence for the formation of *t*-butyl diphenylcyclopropylcarbinyl ether as a primary reaction product in the decomposition of *t*-butyl diphenylcyclopropylperacetate. A sample of this perester (1.6 g from batch (3), p. 389) was subjected to degassed thermal decomposition at 70° in 1.7 M 1,4-cyclohexadiene in cyclohexane. The perester concentration at 70° was initially about 0.086 M. An aliquot of the resulting reaction mixture was analyzed using a weighed amount of diphenylmethane as internal standard. We found (one trace) the following yields for the usual reaction products: 1,1-diphenyl-1-butene, 14%; diphenylcyclopropylmethane, 18%, **B**, 28%, 1-phenyl-3,4-tetrahydronaphthalene, 10%. **B**, it will be recalled, is thought to consist of three reaction products: the above-mentioned *t*-butyl ether; diphenylmethylenecyclopropane, and (isomeric) 1-phenyltetrahydronaphthalenes (p. 71-80). The yield of 28% compares favorably with yields of about 30% for thermal decompositions at 2.7 and 4.9 M 1,4-cyclohexadiene in cyclohexane (Table 2).

The oily residue obtained upon evaporation of the solvent was chromatographed on a column of 75 g Florisil (60-100 mesh) prepared in pentane. Forty 10-ml fractions and ten 20-ml fractions were taken using pentane as eluent, followed by groups of five 20-ml fractions using 2, 5, 10, 20, and 50% diethyl ether in pentane (v/v). Finally, five 20-ml fractions (fractions 76-80) using ether were taken followed by groups of five fractions using 5, 15, 30, and 75% methanol in ether. Visual inspection and analysis of several fractions by vpc (Ucon polar) showed that the hydrocarbon products were concentrated between fractions 20 and 36. Vpc traces of fractions 24, 25, 26, 28, 30, 32, and 34 revealed that some separation of components had occurred, diphenylbutene being concentrated in the early fractions and diphenylcyclopropylmethane, in the later ones. On the other hand, the product **B** and 1-phenyl-3,4-dihydronaphthalene were rather evenly distributed throughout the series. The ratio of these was also rather constant; 1.2 ± 0.2 for the middle fractions. From this we can state that of the original 28% of **B**, only $10 \times 1.2 \cong 12\%$ is eluted with the hydrocarbon products. Either the rest is appreciably more polar material or is destroyed on the column.

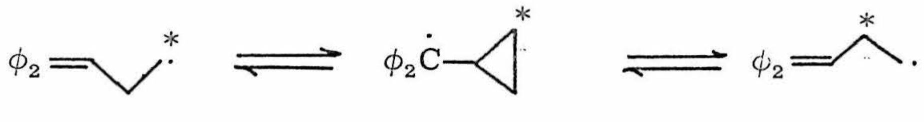
Evidence that the latter alternative is correct was provided by the contents of subsequent fractions. Fractions 70 to 80 (50 and 100% ether) contained appreciable amounts of material. The nmr spectrum of fraction 75 in carbon tetrachloride solution was most revealing. Clearly visible were the highly distinctive resonances of diphenylcyclopropylcarbinol -- a high field doublet due to secondary cyclopropyl protons, split by 6.9 Hz compared to 6.7 for a carbon tetrachloride solution of the authentic material (Aldrich); the singlet hydroxyl resonance at about 1.8 δ; the downfield half of the perturbed quartet due to the tertiary cyclopropyl proton (broad resonances between 0.7 and 2.4 δ obscured the upfield half); and the highly complex aromatic resonances. The vpc trace of the carbon tetrachloride solution of fraction 75 showed a single peak at a retention time of 4.55 min; that of the authentic material in carbon tetrachloride was found to also be 4.55 min.

Fractions 72-79 were combined with a known weight of 1-phenylnaphthalene (retention time about 3.5 min) and analyzed by vpc. The relative peak areas when corrected for the relative sensitivities of the two materials, determined concomitantly for the authentic materials, showed that the combined fractions contained 122 mg of the carbinol, or 11% based on the weight of perester taken.

A lesser amount of material was also concentrated around fraction 66. The nmr spectrum of that fraction in carbon tetrachloride displayed absorbances of the correct shapes and resonance positions for the several types of protons of the ring-opened ether, *t*-butyl (γ,γ-diphenylallyl)carbinyl ether. There was no detectable amount of the analogous ring-opened alcohol in fraction 66. The yield of the ring-opened ether was perhaps 3%, but it is not known whether this material is a primary reaction product or whether it is formed, like the ring-closed carbinol, from the ring-closed ether, either during the thermal decomposition or on the chromatographic column.

Our interpretation of the above observations and the results of other 'large-scale' decompositions (p. 72, 76) is that diphenylcyclopropylcarbinyl *t*-butyl ether is one of the components of **B**.

Thermal decomposition of deuterium-labeled t-butyl (γ,γ-diphenylallyl)peracetate was undertaken in cyclohexane and in the presence of triethyltin hydride to determine whether the two methylene groups in a radical intermediate such as ring-opened **3** could be interconverted via a symmetrical species such as ring-closed **4**. In each



3-α labeled labeled **4** 3-β labeled

case, the experimental procedure was first shown to allow the numbers of relevant hydrogen atoms in the main reaction product to be correctly inferred for decomposition of the unlabeled perester.

Unlabeled Perester in Cyclohexane: One gram of t-butyl (γ,γ-diphenylallyl)peracetate in 55 ml cyclohexane was degassed to 0.2 mm using two freeze-pump-thaw cycles and sealed into a reaction tube (150 ml capacity). The reaction tube was immersed in a bath of refluxing n-octane (bp 125°) for 12 hr. The reaction tube was opened at room temperature, the solvent was distilled, and the residue was chromatographed on Florisil (75 g, 60-100 mesh). Fifty 10-ml fractions were taken using pentane as eluent. Fractions 14-25 were combined and twice distilled bulb to bulb at ca. 0.2 mm (bath temperature ca. 95°). An nmr spectrum of the final distillate was obtained in carbon tetrachloride solution in an A-60 micro cell. The resolution was quite decent. Careful integration gave intensities of 30.9±0.8 for the protons at the 4-position (2.35-2.85 δ) and 35.5±1 for those at the 3-position (1.80-2.35 δ) of 1-phenyl-3,4-tetrahydronaphthalene. When corrected for the methylene protons in 1,1-diphenylbutene, the latter figure becomes 33±1.5, so that the proton populations at the two positions are the same within experimental error.

Deuterium-Labeled Perester in Cyclohexane: One gram of t-butyl (γ,γ-diphenylallyl)peracetate specifically labeled with 1.4_2 g-atoms deuterium in the α-position (p. 385) was subjected to the above treatment. The chromatographic fractions 14-25 were again combined and twice distilled. The composition of the distillate as inferred by vpc was 86% '1-phenyl-3,4-dihydronaphthalene', 3% 'diphenylbutene', 6% '1-phenylnaphthalene', and 5% B [probably labeled tetrahydronaphthalenes (p. 77 , 78)]. Integrated intensities in appropriate resonance regions were corrected for contributions from 'diphenylbutene' and '1-phenylnaphthalene', but not for the 'tetrahydronaphthalenes', whose spectra are not known. Proton populations were calculated assuming 9 aromatic protons in the 'dihydronaphthalene'. The resultant inferences regarding the distribution of deuterium have been given in Fig. 7a, p. 95 .

The present procedure differed from that for the unlabeled perester in that the column chromatography was continued in order to isolate the labeled ring-opened ether 12. Subsequent to the fifty 10-ml fractions, we obtained four 50-ml fractions and then, using 5% diethyl ether in pentane as eluent, six 50-ml fractions. The second of the final six fractions contained most of the product which after distillation in a microapparatus was found by vpc to be 98.5% ring-opened ether. Analysis by nmr gave the following proton populations based on 10 aromatic protons: vinylic, 1.01 ± 0.04, allylic, 1.90 ± 0.04; α to the oxygen function, 0.56 ± 0.04; methyl (in the t-butyl group), 9.23 ± 0.25. This result demonstrates that the perester was originally deuterated in the α-position with respect to the carbonyl function.

Unlabeled Perester in the Presence of Triethyltin Hydride: Details will be given only for the closely similar procedure employed with the labeled perester. The major hydrocarbon reaction product for decomposition in ca. 1 M triethyltin hydride is 1,1-diphenyl-1-butene (Table 10). The ratio of methyl to methylene protons in the recovered diphenylbutene was found by nmr to be 1.55:1.00, in good agreement with the actual 1.5:1.

Labeled Perester in the Presence of Triethyltin Hydride: The reaction was carried out in an apparatus which had two chambers connected by an open tube and connectable by a second route via a break-seal. The deuterium-labeled perester (943 mg) in 10 ml n-octane was placed in one of the chambers. Triethyltin hydride, presently stored in one chamber of a similar two-chambered apparatus, was distilled into the fresh chamber by cooling it in liquid nitrogen while warming the other. n-Octane (5 ml) and 5.4 g of the freshly distilled triethyltin hydride were placed in the second chamber of the reaction vessel. The two halves were jointly degassed to 0.2 mm using three freeze-pump-thaw cycles and the apparatus was sealed off. By this time, the side containing the tin hydride had become cloudy, presumably due to the well-known air oxidation of organotin hydrides (41). Cooling the side containing the perester while warming the other slightly effected the distillation of tin hydride and n-octane into the perester side. A swirling motion was necessary to contain bumping. The tube connecting the two chambers was now sealed off in a gas-oxygen flame. The apparatus was then immersed in a bath of refluxing n-octane for a period of 13 hr.

When the vessel was at room temperature, the reaction-mixture side was opened and 0.5 ml of reaction mixture was transferred to a vial containing a known quantity of 1-phenylnaphthalene. A product analysis was subsequently undertaken by vpc; the results appear in row 11 of Table 10. The reaction vessel was cooled in Dry Ice-acetone, pumped down to 0.2 mm, and again sealed off. The two chambers were now rejoined by breaking the break-seal. The solvent was transferred to the other side by cooling it in liquid nitrogen (boiling point - vapor pressure tables indicate that the C_{16} hydrocarbons of interest should boil at 80 -- 100° at 0.2 mm). A white solid remained. It was twice extracted with 25 ml quantities of boiling pentane. The pentane extracts were filtered and concentrated to a volume of ca. 5 ml, upon which some white solid came out of solution. The whole was poured onto a column of 75 g Florisil prepared in pentane. Thirty 10-ml fractions were taken with pentane as eluent. Those containing the bulk of the hydrocarbon reaction products were combined and distilled bulb to bulb as in the work up of the runs reported above for decomposition in cyclohexane. A nmr spectrum of the distillate in carbon tetrachloride was obtained in an A-60 micro tube. No absorbances other than those expected for the labeled 1,1-diphenyl-1-butene were readily apparent. A careful integration was carried out using five upfield and five downfield sweeps. Integrals for appropriate regions were averaged and corrected for 1.2% of labeled 1-phenyl-3,4-dihydronaphthalene shown to be present by vpc analysis. Proton populations calculated assuming 10 aromatic protons were used directly to compile Fig. 7b, p. 95 .

Interestingly, in both this and the run using unlabeled perester, only traces of diphenylcyclopropylmethane could be found in the fractions from the column chromatography, although the vpc product study on this run (Table 10, row 11) indicated diphenylbutene and diphenylcyclopropylmethane in a ratio of ~11:1. Analysis of the nmr sample indicated only 0.3% of the latter, or a ratio of ~300:1. However, Howden had previously shown diphenylcyclopropylmethane to be a legitimate reaction product for decomposition of the (unlabeled) perester in tri-n-butyltin hydride (by obtaining by preparative gas-phase chromatography a fraction enriched in this material whose nmr spectrum displayed absorbances characteristic of diphenylcyclopropylmethane), so apparently the material is destroyed under the chromatographic conditions.

Air-Induced Decomposition of t-Butyl (γ,γ-Diphenylallyl)-peracetate in the Presence of Triethyltin Hydride. - A n-octane solution 0.08 M in perester and 1 M in triethyltin hydride was made up to determine the feasibility of investigating the kinetics of perester decompositions in triethyltin hydride by monitoring the carbonyl absorbance of the perester at ~1780 cm^{-1} in the presence of the strong, broad Sn-H streaching band of triethyltin hydride at 1813 cm^{-1}. An infrared spectrum obtained on the Perkin-Elmer Infracord Model 237 approximately 10 min after the preparation of the above solution displayed a barely distinct carbonyl absorbance on one slope of the large tin hydride band. The spectrum was measured again 3 hr later under supposedly superior resolution on the Beckman IR-7, but now the carbonyl band was merely a shoulder on the tin hydride band. At 6 hr after preparation of the solution, the spectrum was again obtained on the Infracord; no trace of the carbonyl band could now be discerned. We now, however, noted that a band had appeared at approximately 1650 cm^{-1}, the position previously observed for the carbonyl band in triethyltin (γ,γ-diphenylallyl)peracetate. Rough absorbance measurements indicated a yield of tin ester of about 90% for the 6-hr spectrum.

The reaction mixture was subsequently cooled in an ice bath, upon which white tufts appeared. These were collected by filtration and crystallized from n-hexane to afford triethyltin (γ,γ-diphenylallyl)peracetate (mp 121-123°, melting point on admixture with authentic material undepressed) in 40% yield. The white solid gave infrared and nmr spectra which were in agreement with those of the authentic material.

Subsequent measurements on the rates of the air-induced process were made incidentally to the kinetic determinations of the degassed thermal decompositions discussed below on portions of prepared solutions not required for those determinations. The co-solvent in each case was n-octane. Concentrations differ slightly from those quoted in the legends to Figs. 15 - 18 and in Table 15, since in the latter cases an approximate correction for thermal expansion has been employed.

The reaction mixture for Fig. 18 (0.02 M in perester and 0.72 M in triethyltin hybride) developed the tin ester in 63% yield upon exposure to the air for 4 hrs (as indicated by absorbance measurements at 1651 cm^{-1}). In contrast, one of the degassed samples opened after 3 hr at room temperature gave an apparent yield of tin ester of 5%; but at this point we experienced difficulties in the reproducibility of the base line, so there may actually have been no formation of tin ester.

The reaction mixture of Fig. 17 (1.85×10^{-3} M in perester, 0.44 M in tin hydride) developed the tin ester in yields of 75%, 93%, and 90% after 12, 18, and 36 hr of exposure to the atmosphere at room temperature.

The reaction mixture of Fig. 16 (1.90×10^{-3} M in perester, 0.048 M in tin hydride) indicated yields of 6, 9, and 90% when portions were analyzed after 14, 20, and 74 hr at room temperature.

The reaction mixture of Fig. 15 (2.2×10^{-3} M in perester, 0.0107 M in tin hydride) was maintained in a stoppered flask, after preparation in air, for 5 days. At that time a yield of tin ester of 21% was indicated. After one more day with the flask stoppered, the yield was 30%. The stopper was then left off for one day, after which the yield of tin ester was found to be 92%, and then for a second day, when the yield was 91%.

Several difficulties, such as evaporation of the n-octane and decomposition of the tin hydride (as indicated by deposition of a white solid) over prolonged periods and nonstandard conditions for equilibration of oxygen between the air and the organic solution, make the above observations only semiquantitative. However, it appears that the process is air-induced, that reaction between the air and the tin hydride at least in part generates free radicals, and there is an inhibition period, perhaps representing the consumption of inhibitors or the build up of intermediates involved in the air oxidation. The yields of tin ester may generally be in the range of 85-95%. We argued in subsection 9 (p. 187 , 188) that this indicated that attack of triethyltin hydride on the perester —O—O— bond to give the tin ester was a lower activation energy process that for the alternative attack (see Chart 6, p. 162) to give the tin ether.

Kinetics of Induced Decomposition of t-Butyl (γ,γ-Diphenylallyl)-peracetate in Triethyltin Hydride: The frequency of the infrared transmission minimum for the carbonyl group of triethyltin (γ,γ-diphenylallyl)acetate was determined to be 1651 cm^{-1} by monitoring the transmittance of an 0.01 M solution of the tin ester in n-octane at intervals of 0.5 cm^{-1} over the frequency range 1645-1655 cm^{-1} using the 90-100% transmittance range on a Beckman IR-7. A series of four solutions (0.002, 0.004, 0.006, and 0.010 M) prepared by dilution obeyed Beer's Law when the reference solution was n-octane and when it was 0.2 M triethyltin hydride in n-octane. The average deviation of the absorbance from a visual straight line was 2% in the former case and 6% in the latter. The absorbance readings were obtained, as in the kinetic run for 0.67 M tin hydride and 0.02 M perester discussed below, with reference to an initially set absorbance zero for reference solution in both cells. However, concern was latter encountered with regard to (a) the stability of the instrument over long periods and (b) the reproducibility of the base line as judged by simply removing and then immediately reinserting a cell in the holder. Therefore, in the three kinetic runs at 0.002 M perester, absorbance readings were obtained by recording the 'absorbance' for reference against reference (no attempt being made to adjust the instrument to read identically zero absorbance), of solution against reference, and finally of reference against reference again. The absorbance of the solution was obtained as that the intermediate measurement less the average of the two reference -- reference measurements. A Beer's Law plot for solutions which were 0.0002, 0.0004, 0.0006, 0.0008, and 0.0010 M in tin ester, obtained concomitantly with the kinetic measurements for 0.002 M perester in 0.0097 M tin hydride in n-octane, gave an average deviation of 8% from a visual straight line. We feel that this value represents essentially the reproducibility of the instrument in our difficult observational situation: 1 mm path length, 90-100% transmittance range, slit = 1.5 mm, gain = 3% for the runs at 0.002 M initial perester concentration. Deviations of about this magnitude from optimum first-order lines may be seen in Figs. 15 - 18, pp. 157, 158. For the three runs at 0.044, 0.41, and 0.67 M tin hydride, the absorbance of either 0.01 or 0.001 M tin ester in n-octane was used to relate the limiting absorbancies (A_∞ in eq. 1.9-3) to concentrations, and hence yields, of tin ester arising via induced decomposition of the perester. Yields calculated in this way are shown in Figs. 15 - 18.

Reaction tubes for the kinetic runs were fashioned from lengths of 8 mm pyrex tubing which had been soaked in cleaning solution for one day or more, flushed thoroughly with tap water, scrubbed with Labtone, rinsed well with distilled water and then with acetone, and finally dried at 135° for several hours. For the run displayed in Fig. 17, 14.6 mg of t-butyl (γ,γ-diphenylallyl)peracetate (mp 42.5-43.5°) was weighed into a flask. Into a second flask was weighed 20.92 g of n-octane. Triethyltin hydride stored in a two-chamber evacuated apparatus was freshly distilled as noted under the preparation of the tin hydride. The collection chamber was broken off and 2.947 g triethyltin hydride was weighed into a third flask. The n-octane was now poured onto the tin hydride and the solution was poured between the two flasks a few times to effect mixing. A portion found to weigh 18.53 g was poured onto the perester. The remaining solution was saved to serve as reference solution in the infrared analyses. The flask containing the perester was swirled to dissolve the perester and 1 ml aliquots were transferred by syringe to each of ten reaction tubes which had been constricted at the top for easy sealing. The tubes were quickly attached to a vacuum system by lengths of Tygon tubing, cooled in liquid nitrogen, and degassed to 3×10^{-4} mm using three freeze-pump-thaw cycles. They were then maintained at -80° in Dry Ice-acetone until used (within 48 hr).

Initial concentrations [obtained from the weights recorded above using a specific gravity for triethyltin hydride of 1.25 (our measurement) and for n-octane of 0.704 (91) and assuming no volume change on mixing] were 0.442 M for triethyltin hydride and 1.85×10^{-3} M for the perester. Assuming a standard volume expansion of 12% per 100° temperature rise (p. 390), the concentrations at 110°, the temperature of the thermal decompositions, are 0.41 M and 1.70×10^{-3} M.

The kinetic runs employed a bath of refluxing toluene in a 5-ℓ. flask with a 6 in. diameter opening. The ten reaction tubes were secured by copper wires and lowered en masse into the bath. After a 15, 20, or 30 sec warm-up period, the timer was started and (with the exception of the run of Fig. 15) a first tube was simultaneously pulled and quenched in Dry Ice-acetone. Subsequent tubes were similarly quenched and held at -80° until infrared analysis was undertaken at 1651 cm^{-1}. The procedure for the infrared analysis was given above. At the appropriate time, a tube was warmed to room temperature, shaken to ensure that no separation of components had occurred, and broken at a file mark. The 1-ml quantities of reaction solution usually allowed duplicate analyses for runs of Figs. 15, 16, and 17. The initial concentrations of tin hydride and of perester at 110° (assuming the 12% volume expansion per 100° temperature rise) and the absorbance readings follow [given as reaction time in min, absorbance, absorbance]:

Fig. 15, 0.0097 M, 2.0×10^{-3} M: 10, 0.0062, 0.0059; 25, 0.0094, 0.0101; 40, 0.0128, 0.0130; 60, 0.0187, 0.0208; 80, 0.0245, 0.0264; 130, 0.0326, 0.0364; 180, 0.0362, 0.0364; 310, 0.0373, 0.0385; 550, 0.0370, 0.0376.

Fig. 16, 0.0444 M, 1.75×10^{-3} M: 0, 0.0016, 0.0021; 6, 0.0035, 0.0043; 12, 0.0060, 0.0073; 20, 0.0079, 0.0084; 30, 0.0114, 0.0120; 45, 0.0168, 0.0195; 60, 0.0197, 0.0204; 90, 0.0245, 0.0270; 150, 0.0286, 0.0303; 240, 0.0319, 0.0316.

Fig. 17, 0.41 M, 1.70×10^{-3} M: 0, 0.0230, 0.0217; 2.0, 0.0582, 0.0670; 4.0, 0.0115, 0.0136; 6.0, 0.0129, 0.0173; 9.0, 0.0181, 0.0196; 12, 0.0211, 0.0217; 18, 0.0196, 0.0200; 25, 0.0238, 0.0241; 45, 0.0258; 75, 0.0251, 0.0287.

Fig. 18, 0.67 M, 0.018 M: 0, 0.0023; 3.0, 0.0112; 6.1, 0.0176; 8.0, 0.0217; 12.0, 0.0282; 20, 0.0323; 32, 0.0322; 112, 0.0313.

The absorbance readings listed for Fig. 15 are uniformly lower than those directly measured by 0.0015; the reference solution in that case was *n*-octane, rather that 0.1 M triethyltin hydride in *n*-octane, and the tin hydride does absorb slightly at 1651 cm^{-1}.

The absorbance-time data was fitted in each case to eq. 1.9-3, p. 159,

$$A(t) = A_\infty - (A_\infty - A_0) \exp(-k_T t)$$

using the generalized least-squares formalism of Section Two, subsection 2. A_∞, A_0, and k_T were treated as adjustable parameters. The following results were obtained: Fig. 15 -- $A_\infty = 0.0387 \pm 0.0008$, $A_0 = -0.0006 \pm 0.0012$, k_T (min^{-1}) $= 0.0130 \pm 0.0010$, RUSD (relative unbiased standard deviation, given by the square root of the sum of the squares of the deviations between observed and calculated absorbance readings divided by the number of absorbance readings fitted less one) = 0.0015; Fig. 16 -- $A_\infty = 0.03314 \pm 0.0008$, $A_0 = 0.0012 \pm 0.0053$, $k_T(\mathrm{min}^{-1}) = 0.0150 \pm 0.0011$, RUSD = 0.0011; Fig. 17 -- $A_\infty = 0.0254 \pm 0.0009$, $A_0 = 0.0023 \pm 0.0012$, $k_T(\mathrm{min}^{-1}) = 0.128 \pm 0.017$, RUSD = 0.0018; Fig. 18 -- $A_\infty = 0.0327 \pm 0.0009$, $A_0 = 0.0011 \pm 0.0017$, $k_T(\mathrm{min}^{-1}) = 0.138 \pm 0.015$, RUSD = 0.0013 .

In forming the weighing factors L after the fashion of eq. 2.2-14, p. 214, we have assumed a standard error of 0.3 min in each of the quoted reaction times; this quantity principally represents the uncertainty in the effective warm-up periods. In addition, we have equated the standard error in the absorbance readings to the value of RUSD from the previous iteration.

The curved lines in Figs. 15 - 18 were drawn up using the least-squares estimates given above. To prevent overcrowding, duplicate infrared analyses were averaged for plotting. The reader will note that A_0 is usually slightly positive. The apparently finite initial absorbance appears to be due to the perester itself; an 0.02 M solution in n-octane gave an absorbance of 0.01 in the 1 mm cells at 1651 cm^{-1}.

Translation of the A_∞ into yields of the tin ester suffers from uncertainties in the A_∞, in the preparation of and absorbance measurements on standard solutions, and in the determination of the initial quantity of perester taken, always approximately 15 mg. The yields quoted in Figs. 15 - 18 are probably good to not better 10-15% (relative).

According to the mechanistic scheme of subsection 9 to Section One, the concentration of triethyltin hydride consumed in the induced decompositions should be 1-2 times the initial perester concentration. This was checked in the case of the run displayed in Fig. 15, where the ratio of initial concentrations of triethyltin hydride (0.0107 M, at room temperature) and perester (2.2×10^{-3} M at room temperature) was smallest. We found the tin hydride concentration in the tube opened at 550 min to be 0.0088 M, or 1.9×10^{-3} M less than the initial concentration. This gives at least partial assurance against the general incursion of additional mechanistic steps which might result in wholesale decomposition of the triethyltin hydride.

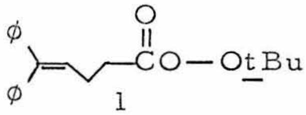
Kinetics of Thermal Decomposition of t-Butyl Diphenylcyclopropylperacetate in Cumene. - A solution of ca. 0.1 M perester in cumene was allowed to stand exposed to the air at 73° F (23°C) in a thermostated room. Disappearance of the perester was monitored by recording the infrated spectra of aliquots between 1850 and 1700 cm^{-1} on the Perkin-Elmer Infracord Model 237. This was done at an arbitrary time zero (about 5 min after preparation of the solution), 20, 40, and 270 min later, and after 18 hr. The absorbance readings at the carbonyl maximum of the perester were measured with respect to a valley at 1790 cm^{-1} which appeared between the carbonyl band and a small peak at 1800 cm^{-1} (which itself appeared to be constant throughout the run). The absorbance readings were, in order of increasing time, 0.475, 0.440, 0.377, 0.084, and 0.024. The latter value was taken to be the infinity absorbance, A_∞, in the equation shown below. The data were fitted to the equation

$$A(t) - A_\infty = (A_0 - A_\infty) \exp(-k_0 t)$$

according to the least-squares formalism described in Section Two, subsection 2, where A_0 and k_0 were treated as adjustable parameters. The results have been discussed (pp. 236-240).

Viscosities of several liquids and binary mixtures were determined at 20° using a modified Ostwald viscometer (cleaned in cleaning solution) in conjunction with a constant temperature bath. Flow times for 10-ml quantities of cyclohexane (η = 0.960 cp) and benzene (η = 0.648 cp) were employed to determine the cell constants (161). In general, ten measurements of the flow time were made on each solution. Times were reproducable to three or four parts per thousand. The viscosity of freshly distilled 1,4-cyclohexadiene was found to be 0.595 cp. For mixtures of 1,4-cyclohexadiene and cyclohexane in the proportions (v/v) of 1:7, 1:3, and 1:1, viscosities of 0.845, 0.778, and 0.679 cp, respectively, were found. Freshly distilled indene of the same grade as that used in the perester decompositions (p. 372) gave a flow time corresponding to a viscosity of 1.76 cp. Viscosities of 0.28 and 0.50 cp were found for diethyl ether and tetrahydrofuran. The literature value for the former is 0.233 at 20° (162); the poor agreement suggests that inferred viscosities which lie outside the range of viscosities of the standard materials (benzene and cyclohexane) may deviate systematically from the true viscosities. The viscosity of tetraethyltin was found to be 0.63 cp.

STRUCTURES AND NUMBERS OF COMPOUNDS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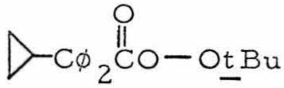
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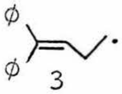
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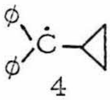
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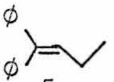
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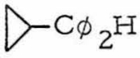
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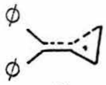
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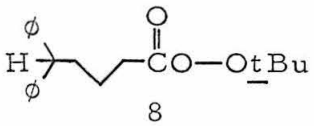
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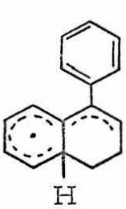
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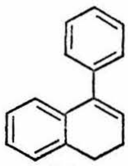
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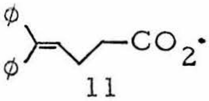
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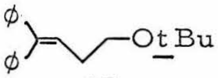
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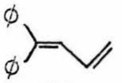
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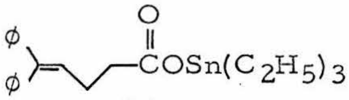
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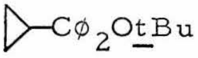
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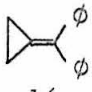
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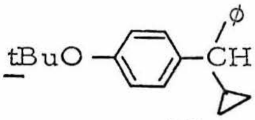
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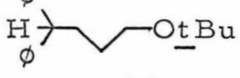
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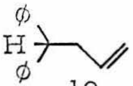
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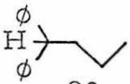
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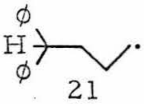
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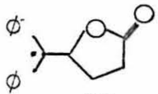
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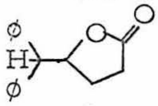
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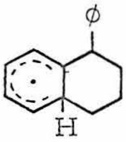
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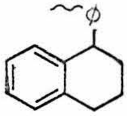
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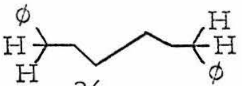
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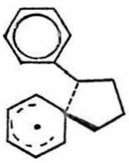
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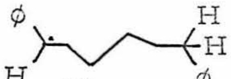
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PROPOSITION NO. 1

Abstract

A reinvestigation is proposed of the important work of Waits and Hammond on the experimental separation of primary and secondary recombination in cage processes. Systems are suggested which may be more amenable to a definitive result than we believe is that employed by Waits and Hammond.

Discussion

Whenever pairs of radical fragments are produced in solution via thermal or photochemical dissociation reactions, the possibility exists that cage reaction may occur--that the particals may for example (re)-combine instead of diffusing apart. Two types or stages of cage reaction are distinguished theoretically: (a) Primary recombination, in which the particles react without ever attaining a separation of more than a molecular diameter in excess of the sum of the molecular radii; and (b) Secondary recombination, in which reaction occurs following a period of essentially free diffusion (1).

Workers in the field have shown a lively interest in the question of whether cage recombination can occur with substantial probability if particles become separated by one or more layers of solvent molecules, as is pictured for secondary recombination, or whether one simply has collapse of the initial solvent cage after perhaps 10^{-11} or 10^{-12} sec to give either the cage product or separated radicals. Braun, Rajbenbach, and Eirich have argued that the former is correct for formation of ethane in the thermolysis of acetyl peroxide (2). The decomposition of acetyl peroxide appears to occur by scission of the –O–O– bond to give a pair of acetoxy radicals which may combine or decarboxylate in competition with diffusive separation (3). After both acetoxy radicals have decarboxylated, the derived methyl radicals may combine to form ethane. By studying the effect of viscosity for reaction in a series of hydrocarbons on the cage yields of ethane and methyl acetate (which may be formed while only one of the acetoxy radicals has decarboxylated), Braun *et al.* were able to infer a rate constant of about 2×10^9 sec^{-1} for decarboxylation of acetoxy radicals at 65° (2). They also inferred an average initial separation of methyl radicals of about 50 A in *n*-octane, where the yield of cage ethane is about 6%. Most of the cage ethane is undoubtedly formed in decomposition events in which the methyl radicals are initially separated by considerably less than this average distance, but the implication is clear that diffusive recombination is possible. Unfortunately, the necessity for rather extensive approximations in their treatment makes this result of unknown validity.

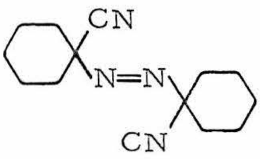
Noyes has studied quantum yields for production of free iodine atoms from photodecomposition of molecular iodine in solution (4). The quantum yields are always less than unity, and the deviation from unity is ascribed to cage recombination of iodine atoms. By treating the solvent as a viscous continuum, Noyes was able to estimate the mean interatomic distance attained by atoms separating with excess kinetic energy before essentially free diffusion becomes possible. For 4047 A light in hexane solution, this distance is calculated to be about 4 A over and above the sum of the radii for two iodine atoms, and 17% of decomposition events are observed to result in cage recombination. For light of longer wavelengths and decomposition in a considerably more viscous solvent, the calculated separations are only a few tenths of an angstrom, but the process at 4047 A in hexane would seem to involve secondary rather than primary recombination.

Waits and Hammond have concluded that coupling of caged α-cyanocyclohexyl radicals in chlorobenzene solution occurs by primary rather than secondary recombination (5). They compared the effect of added radical scavengers (bromine, iodine, 1, 1-diphenyl-2-picrylhydraxyl (DPPH)) on the efficiency of the cage combination with the predictions of a theoretical model due to Noyes (6) which assumes random diffusion of the radical pair during the time in which cage reaction may take place (i. e., that the cage process involves secondary recombination). If ϕ is the probability that the molecular pair, which otherwise would have recombined, instead reacts with scavenger, then Noyes' theory predicts that

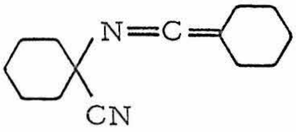
$$\phi \cong 2a(2\pi k_s(S))^{\frac{1}{2}}$$

where a is a constant, (S) is the concentration of added scavenger, and k_s is its rate constant for reaction with the caged radical species. Thus, a plot of the efficiency of formation of cage product in the presence of scavenger, $1 - \phi$, against the square root of the scavenger concentration should yield a straight line with an intercept of unity.

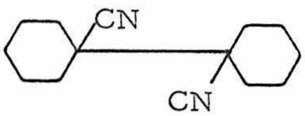
Waits and Hammond tested this expectation for thermal decomposition of N-(1-cyanocyclohexyl)-pentamethyleneketenimine (RR') in the presence of DPPH (Fig. 1) and of 1, 1'-azocyanocyclohexane (RN_2R) in the presence of bromine and iodine (Fig. 2). In Fig. 2 only the



RN_2R



RR'



RR

bromine scavenging results are shown, but we should note that those for iodine define an almost indistinguishable line. In each case, the intercept of the straight line is about 1. 1 rather than 1. 0. In contrast, plots of 1 - ϕ against the first power of the scavenger concentrations did give good straight lines with intercepts of unity.

Another point of interest is that extensive interference with cage recombination is not observed at scavenger concentrations of *ca* 10^{-2} M as predicted by Noyes (1), but only at much higher concentrations where, Waits and Hammond argue, interference with primary recombination seems unavoidable. They suggested (a) that their case either involves primary recombination or that primary and secondary recombination are not experimentally separable and (b) that a scavenger can compete with the cage process only if it happens to constitute one of the solvent molecules making up the cage wall. A treatment suggesting that this circumstance should lead to the observed linear scavenging relationship was presented.

If correct, this conclusion is of great significance regarding the nature of diffusive processes in solution. However, we feel that several important experimental and interpretational ambiguities prevent

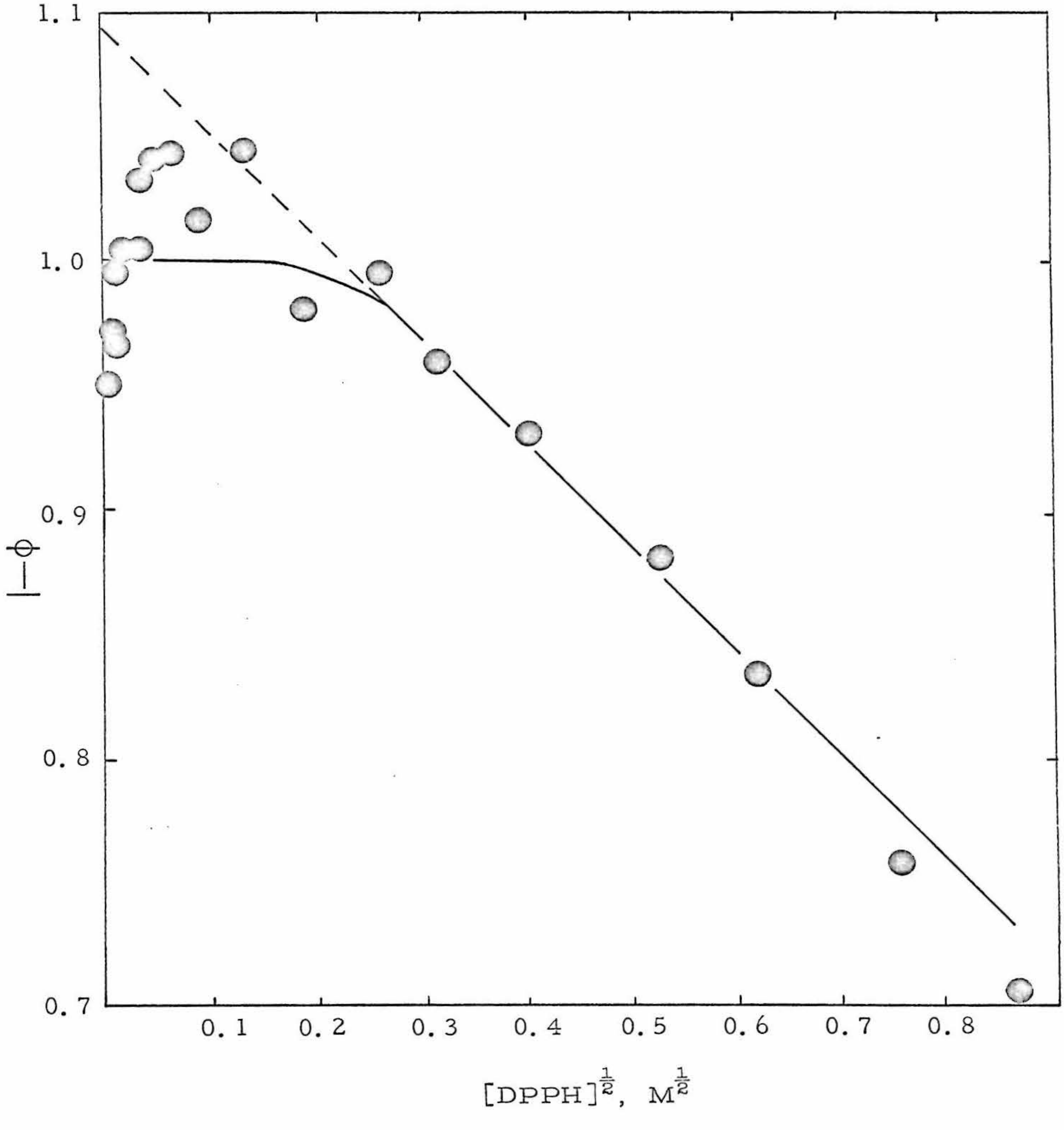


Figure 1. Dependence of relative cage efficiency on the square root of the DPPH concentration for RR' decomposition by Waits and Hammond (5).

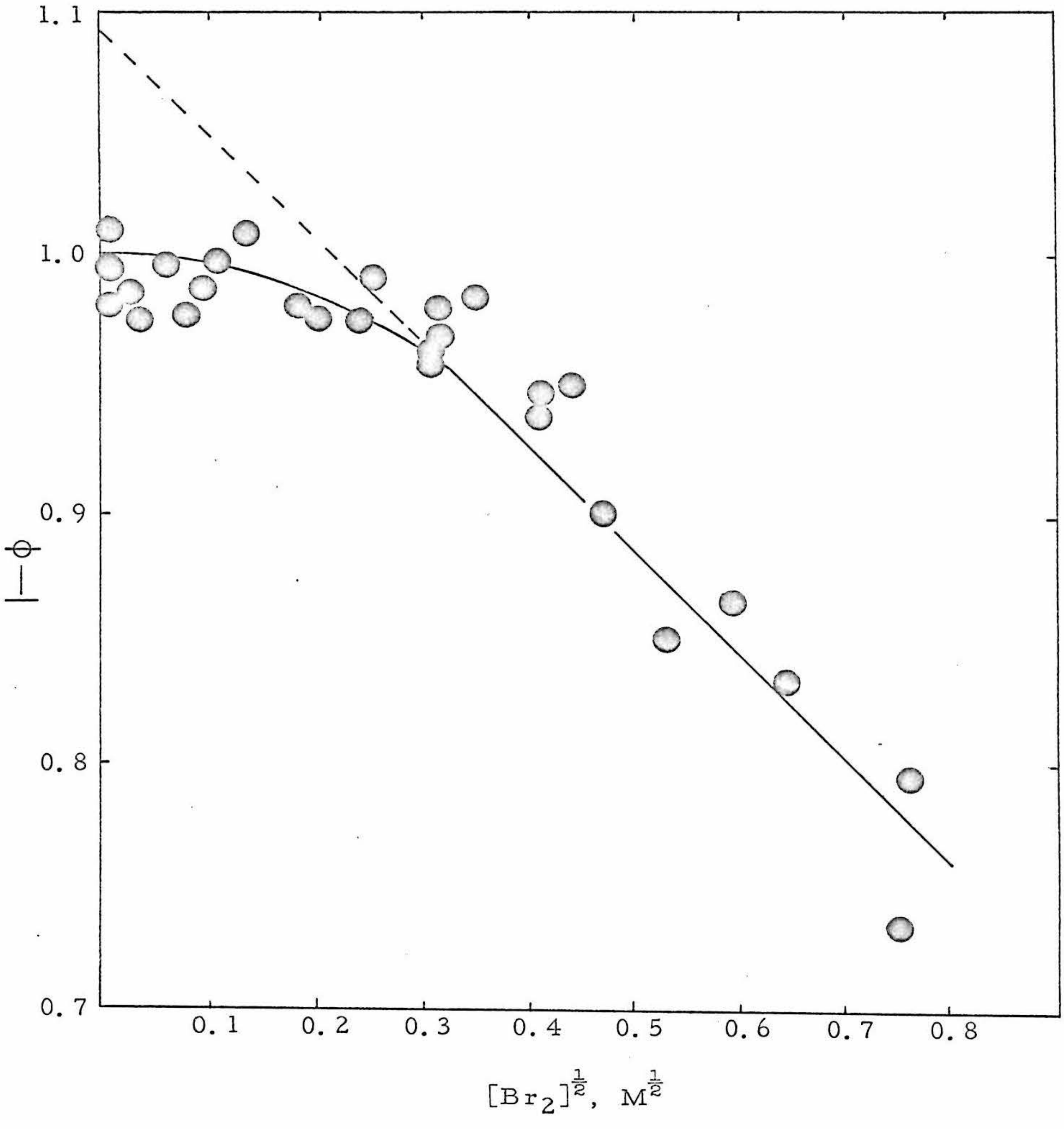


Figure 2. Dependence of relative cage efficiency on the square root of the bromine concentration for RN_2R decomposition by Waits and Hammond (5).

ready acceptance of this conclusion. The nature of one such ambiguity can be seen in Fig. 1. The abscissa in that figure is essentially linear in the yield of the cage product, 1,1-dicyanobicyclohexyl (RR); the value $1 - \phi = 1.0$ corresponds to a 27% yield of RR. Thus one can see that the yield of RR increases with decreasing (DPPH) and reaches a maximum of about 29% for $(\mathrm{DPPH})^{\frac{1}{2}} = 0.05$ (5). As the DPPH concentration is further reduced, however, the yield of RR decreases with striking regularity to a value of about 24% (5). A natural explanation for situations of this type would be that as the concentration of the radical scavenger is continually decreased a point is reached at which once-formed RR begins to be attacked by radicals produced in subsequent decomposition events. But the initial concentration of the radical source, RR' in this case, was only about 1.7×10^{-5} M, and it is difficult to accept the suggestion that some radical intermediate will attack RR in preference to the chlorobenzene solvent when the concentration of the latter is about 10^{6} greater than that of the former.

In any case, the yield of RR does vary appreciably at low scavenger concentrations. Waits based his interpretation of the data on the assumption that a 27% yield of RR signifies the absence of cage scavenging. If one instead adopts a value of 29%, the effect is to relabel the abscissa in such a way that the dotted extension of the solid line in Fig. 1 comes very close to $1 - \phi = 1.0$. If correct, this would obviate Waits' conclusion that the square root relationship predicted by Noyes assuming a secondary recombination mechanism fails.

No such obvious reinterpretation can be suggested for the bromine (or iodine) scavenging results (Fig. 2). However, in both this and the above case, the necessity of using scavenger concentrations on the order of 1 M introduces the possibility that medium effects may substantially influence the yields of RR which would be formed in the absence of scavenging of the caged radicals. The following comparison is relevant in this regard. Schuler (7) has reported that the rate constant for reaction of methyl radicals with iodine is a factor of 16 greater than that for reaction of methyl radicals with the stable free radical galvinoxyl (8). However, Bartlett and Funahashi have found that galvinoxyl reacts with cyanoisopropyl radicals ten times as rapidly as does iodine (8). If we assume that cyanoisopropyl radicals do not react with galvinoxyl more rapidly than do methyl radicals, we conclude that methyl radicals react with iodine at least 160 times as rapidly as do cyanoisopropyl radicals.

Cyanocyclohexyl radicals and cyanoisopropyl radicals should be of closely similar reactivity. If Schuler's and Bartlett's work are correct, this would suggest first of all that reaction of cyanocyclohexyl with iodine (and also with bromine and DPPH) may not be sufficiently rapid to support the inference of Waits and Hammond that reaction of a caged cyanocyclohexyl radical with an adjacent iodine molecule will occur with high probability. Secondly, the implication is that scavenging of methyl radicals from azomethane decomposition (photolytic if this is possible in the presence of iodine or bromine) may be possible with scavenger concentrations of 0.01 to 0.1 M. If so, any worries about medium effects could be dispensed with.

It is therefore suggested that the essentials of the work of Waits and Hammond be repeated using azomethane or an azo compound yielding radicals of reactivity comparable to methyl radicals (such as cyclopropyl or vinyl radicals). In addition, use of optically active azo compounds yielding substituted cyclopropyl (9) or vinyl (10) radicals would permit simultaneous investigation of the residual optical activity in the cage coupling product formed in the presence of varying amounts of scavenger. Such a study could in principle yield additional information regarding the behavior with time of the probability per unit time that the caged radicals recombine. Noyes' relationship (6) assumes an initial rapid buildup of this probability (which may be thought of as a time-dependent rate constant for cage reaction), followed by a decay with $t^{-3/2}$ as the radical pair is increasingly separated by diffusion. It might be possible to partially test this time behavior, provided that the results do not strongly confirm the conclusion of Waits and Hammond that secondary recombination is unimportant.

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PROPOSITION NO. 2

Abstract

From the standpoint of computation time, the problem of orbital exponent optimization in even minimum-basis-set SCF Hartree-Fock calculations is a vexing one. We suggest that it may be possible to employ derivative aspects of a calculation using trial exponents, such as a Mulliken population analysis, in the exponent optimization. A reasonably good correlation of net charge on hydrogen with optimized hydrogen exponent is cited for a series of eight hydrides in partial support of the proposal.

Discussion

With the advent of flexible and reasonably rapid programs for the calculation of multicenter molecular integrals, it has become possible to carry out SCF calculations within the SCF Hartree-Fock LCAO framework on a variety of polyatomic molecules. Because of present limitations in the molecular integral calculations and the generally rapid increase in computation time with increased complexity of the molecular system, such calculations have mainly employed minimum basis sets when Slater-type orbitals have been used. With the minimum basis set restriction, it seems especially necessary to make each orbital as suitable as possible by optimization of all orbital exponents.

There are several possible approaches to the problem of exponent optimization. One would be to employ the formalism of eqs. 2.2-3 to 2.2-6 of this thesis (pp. 209, 210), where the function S would be interpretated as the molecular energy. Ransil has employed such an approach for a series of monohydrides (those in Fig. 1) (1), where the necessary derivatives with respect to the orbital exponent parameters were evaluated numerically. He was guardedly optimistic about the general feasibility of his approach. However, it can be shown that $2n^2 + 1^*$ calculations are required for each successive trial optimization (see p. 211), three to five of which were required in Ransil's work. Thus, the number of calculations required to effect the optimization rises discouragingly steeply with increasing complexity of the molecular system. In addition, it is doubtful that the accuracy required for numerical stability could be attained for complex systems where one must contend with round off error and errors due to the approximate evaluation (perhaps to one part in 10^5 or 10^6) of large numbers of molecular integrals.

A similar approach has been advanced for Gaussian-type orbitals in which formulas for analytic evaluation of the necessary derivatives are given (2). We are unaware of whether the scheme is feasible for Gaussian orbitals or whether it can be extended to Slater-type orbitals.

Exponent optimizations for polyatomic systems have employed what may be called the brute-force method. This consists in cyclically optimizing the exponents by calculating the energy for a trial value and for incremented and decremented exponent values and determining the energy minimum by a parabolic fit (3, 4, 5, 6). For BH_3 where there are four independent exponents, optimization required some 45 separate

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*The value of n is given by the number of independent exponents.

calculations having a computation time of 5 minutes each (3). Clearly such circumstances place rather severe limitations on any hopes for rigorously optimizing exponents for the more complicated systems which have been treated by calculations of the type under consideration (7), at least for the present generation of computers.

We suggest that it may be possible to employ results from a current computation which are only indirectly related to the molecular energy to optimize the exponents or at least to enable cyclic optimization to be begun with better approximations to the exponents than would otherwise be possible. Specifically, we suggest that an approach of the general type which underlies the Slater rules (8), in which the concept of mutual shielding of the electrons is employed, may be feasible. We would however seek to evaluate the effect of shielding in each case for the wave function obtained using trial exponents, perhaps employing elements of a Mulliken population analysis (9).

Slater rules suggest effective nuclear charges of 3.25 for the 2s and 2p orbitals of neutral carbon, 3.60 for C^+, and 2.90 for C^- (8). We believe that a correlation of orbital exponent with charges on atoms in molecules may be generally useful. In Fig. 1 such a correlation is investigated for hydrogen atoms in hydrides where the net charge on hydrogen is 1 − the gross atomic electron population (9). The monohydrides were calculated by Ransil (1), except for H_2 (10). The BH_3 calculation is due to Palke and Lipscomb (3), CH_4 is due to Pitzer (4), and H_2O, to Pitzer and Aung (5). The correlation is especially good for the monohydrides, CH_3 and H_2O deviating somewhat from a line which could be drawn through the other points. Still, we feel that results are encouraging. Extension to atoms contributing several orbitals to the minimum basis set would be more difficult; perhaps the major and most sensitive changes from exponents given by Slater rules would however be found for the valence-shell electrons. Effects on the orbital exponents due to the presence of neighboring atoms might conceivably be expressable in terms of overlap populations (9).

It is uncertain just where such an investigation would lead, but the potential value is, we feel, sufficiently great to warrent the attempt.

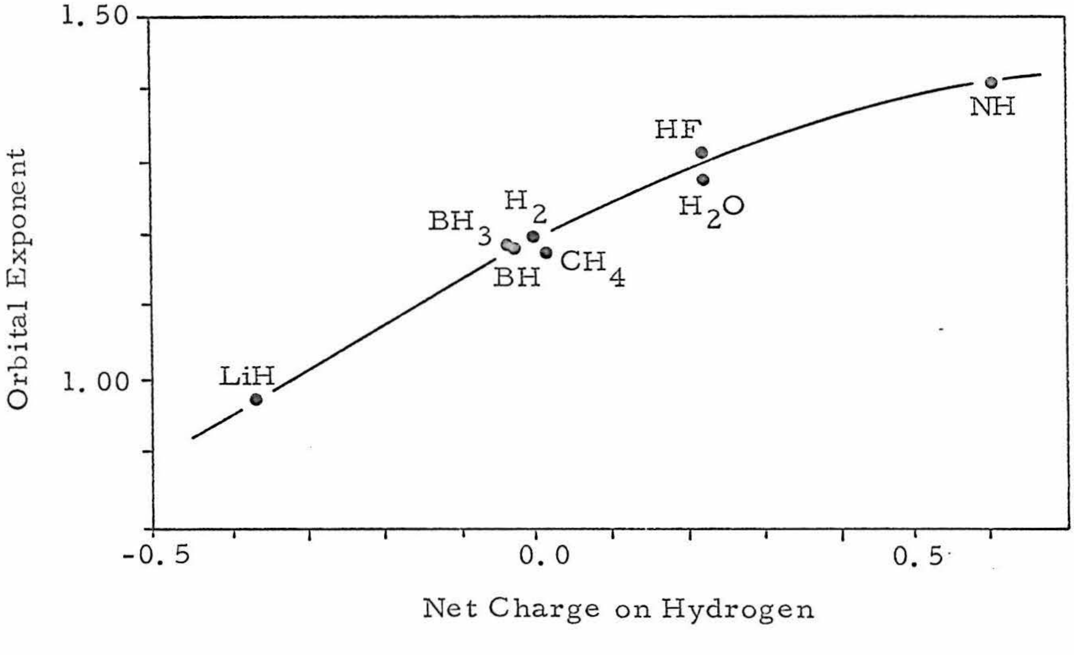

Figure 1. Correlation of exponent for 1s Slater-type orbital on hydrogen with calculated net charge on hydrogen in minimum-basis-set fully optimized SCF LCAO MO calculations.

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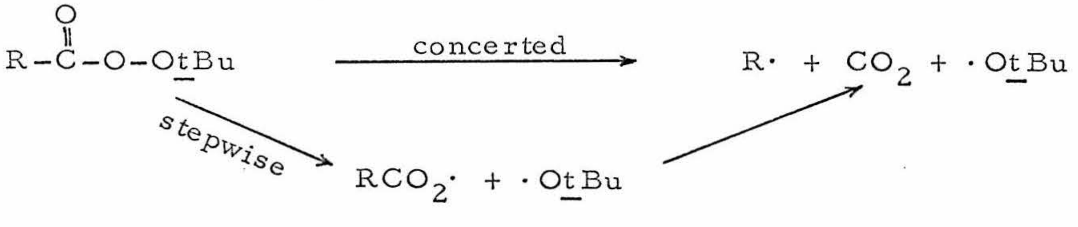
PROPOSITION NO. 3

Abstract

The decomposition of t-butyl peresters, RCO_2Ot-Bu, proceeds by a concerted two-bond scission when the derived radical R· is as or more stable than a secondary alkyl radical, but apparently by simple scission of the –O–O– bond when R is methyl. It is suggested that peresters decompose by a superposition of the two kinds of processes when R is primary alkyl and that this can be demonstrated via a kinetic deuterium isotope effect.

Discussion

Extensive kinetic investigations of the rates of thermal decomposition of t-butyl peresters, RCO_2Ot-Bu, have now been reported. Half-lives at 100° for decomposition in chlorobenzene (and literature references) are given in Table 13, p. 51 of this thesis. The variation of a factor of nearly 10^5 in the half-lives between the fastest and the slowest signifies a major dependence, under certain conditions at least, of reaction rate on the stability of the derived radical R·. This indicates that the more reactive peresters decompose primarily by the concerted pathway in which R· is largely formed in the decomposition transition state.

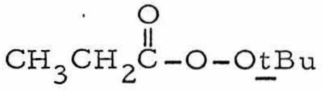


However, it may still be that the less reactive peresters decompose by the stepwise mechanism with initial scission of only the –O–O– bond. This possibility was briefly explored earlier in this thesis (Section One, subsection 3). We suggested there that the regular decrease in D(C–H) for successive substitution of methyl groups for hydrogen atoms in methane (1) should lead to a geometric progression of decomposition rates for a series of peresters where R is methyl, ethyl, isopropyl, and t-butyl, if the decomposition is concerted in all of these cases. Actual relative rates at 110° relative to methyl = 1.00 are: long chain primary aliphatic, 1.6 to 1.8; isopropyl, 17; t-butyl, 200. If we take the decomposition rate of the perester with R = ethyl to be the same as the mean of those with R = long chain primary aliphatic, we see that the second substitution of methyl for hydrogen on methane increases the rate of decomposition by a factor of ten and the third substitution effects an additional increase of a factor of twelve. The first substitution, on the other hand, increases the decomposition rate by less than a factor of two.

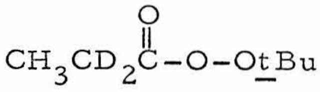
Trachtmann and Miller, the researchers who investigated the long chain primary aliphatic peresters, took this modest rate increase to indicate that the decomposition is stepwise both in their cases and for R = methyl (2). But this interpretation need not be correct. It might be that concerted decomposition is much slower than stepwise decomposition for R = methyl, but that the rate of the former is greatly increased for R = ethyl or primary aliphatic, whereas the rate constant for simple –O–O– bond scission is scarcely effected. The result could be a modest increase in the sum of the rates of the two processes.

An entirely reasonable rate sequence can be constructed if it is assumed that approximately 0.98 units of each of the relative rates quoted above arises via –O–O– scission and that the rest (0.02 for methyl, 0.7 for ethyl or primary, 16 for isopropyl, and 199 for *t*-butyl) represents the contribution of the concerted process. Thus, approximate relative rates for *concerted* decomposition would be: methyl, 1.00; ethyl, 0.7/0.02 = 35; isopropyl, 800 = 35 × 23; *t*-butyl, 10,000 = 800 × 12.

We suggest that the perester with R = methyl decomposes essentially by simple scission of the –O–O– bond and that peresters where R is as or more stable than a secondary alkyl radical decompose mainly by the concerted breaking of two bonds, but that the two processes are of approximately equal importance for R = ethyl or primary aliphatic. We further suggest that this interpretation can be tested by measuring and comparing the decomposition rates for I and II.

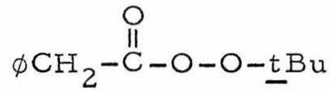

$CH_3CH_2\overset{\overset{O}{\|}}{C}\text{-O-O}\underline{t}Bu$

I


$CH_3CD_2\overset{\overset{O}{\|}}{C}\text{-O-O}\underline{t}Bu$

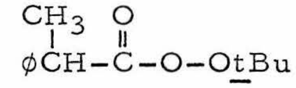
II

A number of secondary kinetic isotope effects have been measured for systems in which a tetrahedrally hydridized carbon is converted to a free-radical center. This is the type of transformation which takes place for decomposition of I or II if the concerted pathway is followed. Rate constant ratios (k_H/k_D) for such processes fall into the range 1.13 to 1.17 per α-deuterium (3). Especially pertinent are the values k_H/k_D = 1.17 per α-deuterium in labeled III and 1.14 per α-deuterium in labeled IV, both peresters which from their reactivity (Table 13, p. 51) surely decompose by the concerted pathway (3a). On the other hand,



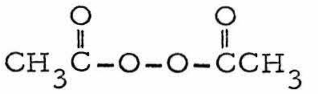
$\phi CH_2-\overset{O}{\overset{\|}{C}}-O-O-\underline{t}Bu$

III



$\phi \overset{CH_3}{\overset{|}{C}}H-\overset{O}{\overset{\|}{C}}-O-O\underline{t}Bu$

IV



$CH_3\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}CH_3$

V

massively labeled acetyl peroxide (V, 85% d_6), reliably established to undergo simple –O–O– scission (4), decomposed at a rate which was within one or two percent of that of unlabeled acetyl peroxide (3a). Thus, deuterium substitution has negligible effect on the rate of formation of acyloxy radicals.

If I undergoes about 40% concerted and 60% stepwise decomposition, as we anticipate, the secondary isotope effect should be about $1.15 \times 0.4 + 1.00 \times 0.6 = 1.06$ per deuterium, and k_I/k_{II} should be about $1.06^2 = 1.12$. If not significant amount of concerted decomposition occurs for I, k_I/k_{II} should be about 1.00.

A difference in decomposition rate of 12% could be detected by measuring k_I and k_{II} by standard techniques (such as by infrared), but it may be more satisfactory to use a competitive technique. Thus one would subject a solution containing known amounts of I and II to partial decomposition, isolate the unchanged perester, and analyze the isolated material for deuterium content, perhaps by nmr spectroscopy. If I and II are initially present in equal concentrations and k_I/k_{II} is 1.12, after three decomposition half-lives for I, 12.5% of I and 15.6% of II would be unchanged. Thus the ratio of II:I would be 1.25, or 25% greater than initially. Similarly, after five half-lives the ratio of II:I would be 1.46. The molecular weights of I and II are sufficiently low that isolation via distillation and other procedures should be possible at temperatures at which the peresters are thermally stable.

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PROPOSITION NO. 4

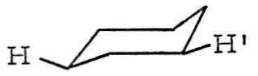
Abstract

Two mechanisms have been proposed to account for the observation of long-range proton spin-spin coupling across four bonds in saturated cyclic systems. A third is suggested, and experiments are proposed to lend support to this one for couplings across five saturated bonds which will be sought in the experiments.

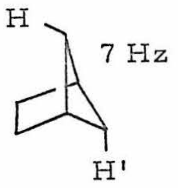
Discussion

There have now been a number of reports of measurable proton spin-spin couplings across four saturated bonds. In rigid but unstrained systems such as I, coupling constants, $^4J_{HH'}$, of magnitude 1.0 to 2.2 Hz have been observed between equatorial protons (1). In a number of highly strained substituted bicyclo(2.1.1)hexanes (II), four bond couplings of 6 to 8 Hz have been reported (2). And in the even more highly strained bicyclobutane (III) and bicyclo(1.1.1)pentane (IV), four bond couplings of 10 to 18 Hz have been observed (3). In one case (V), a coupling formally through five saturated bonds has been found (4).

Two suggested explanations of the origin of the four-bond couplings have appeared in the literature. Using a semiempirical valence-bond treatment, Barfield (5) has predicted that the four-bond case should show an angular dependence reminiscent of that found by Karplus (6) for vicinal coupling constants. The magnitude of the



I



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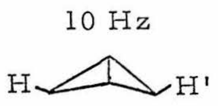

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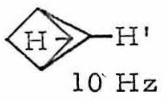

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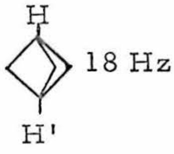

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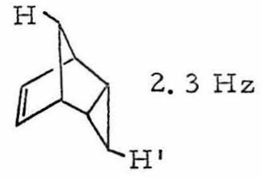
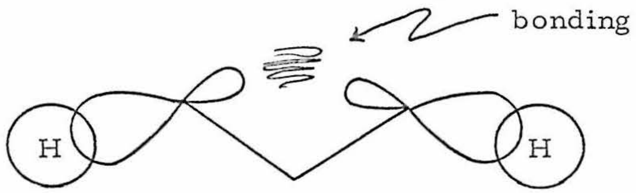


V

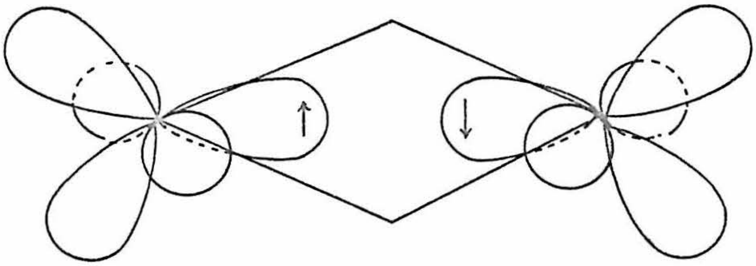
coupling is predicted to range from about -0.4 to + 1.2 cps. This is of the same order of magnitude as the couplings which have been reported in systems like I, but is smaller--possibly significantly so--than those observed for II–IV. Meinwald and Lewis (2a) earlier had suggested that ${}^4J_{HH'}$ couplings might occur through overlap between the small lobes of the orbitals directed 180° away from the directions of the 1,3 carbon to proton bonds, and thus pointing toward each other.



Our suggestion is that the presence of significant ring strain is the factor which makes possible large long range couplings such as depicted above. We picture the role of ring strain as being to increase the importance of non-perfect-pairing structures, some of which have, for example, a bond between the carbon atoms to which the remote hydrogen atoms of interest are bound.

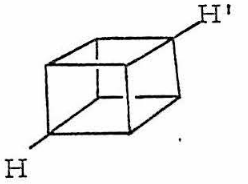
The bonding in cyclopropane has been discussed by a number of authors (7). Walsh suggested a model in which each carbon is sp^2-p hybridized with a trigonal hybrid from each carbon directed toward the center of the ring (7a). For our purposes, this is the most convenient picture. The important concept, stressed in the Coulson-Moffitt 'banana'bond' model as well (7b), is that significant deviations from perfect pairing are to be expected in strained saturated cyclic systems.

Cyclobutane is another example of such a situation. Here, a Walsh-type of model would provide a rationalization for a direct transfer of spin information between 1, 3 carbon atoms (although this has not yet been observed):

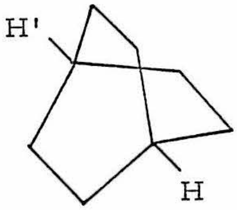


It is not suggested that such a model is a fully adequate description of the bonding in cyclobutane, but only that the angle strain provides a driving force (which must be sought quantum mechanically) for the introduction of <u>some</u> character of this type. However it is described, the basic effect in the transfer of spin information is presumed to arise from deviations from perfect pairing.

It is proposed that there will be a measurable five-bond coupling in cubane (VI) arising through some direct bonding between apex carbon atoms which permits more efficient transfer of spin information than is possible through the intervening carbon-carbon bonds. The overall effect would presumably work through an intra-atomic Hund coupling between electron spins similar to that discussed by Koide and Duval (8). It is further proposed that the formal five-bond coupling in VI be compared with that in bicyclo-(2. 2. 2)-octane (VII).



VI



VII

The five-bond couplings would be sought in each case in the ^{13}C satellites of material deuterated at all positions but the two of interest. In the case of cubane, the synthesis would follow that of Eaton and Cole (9), starting with fully deuterated 2-cyclopentenone. The apex protons would be introduced during the two perester decompositions required. Bicyclo-(2. 2. 2)-octane fully deuterated in the methylene positions would be synthesized from the di-t-butyl perester of d_{12}-bicyclo-(2. 2. 2)-octane-1, 4-dicarboxylic acid. The deuterated dicarboxylic acid would be prepared by the method of Roberts, Moreland, and Frazer (10) from ethylene dibromide-d_4 and diethyl 3, 3, 4, 4-d_4-succinate.

The apex inter-atomic distance in VI has been determined by x-ray crystallography to be 2. 69 A (11). That in VII should be

$1.54 + 2(1.54)\sin(19.5^\circ) = 2.57$ A. As there should be no appreciable angle strain in VII, the bonding should be essentially sp^3. In VI, however, the C-H bonds are expected to have more than 25% s-character. The amount could be estimated from the ^{13}C-H coupling constant determined in the experiments. At the same internuclear distance, the result of the difference in hybridization will be to make overlap between the backside lobes more favorable in bicyclooctane. This prediction is simply a manifestation of the well-known fact that increasing admixture of s with p character increases the directionality of the resulting hybrid (12).

Thus, both by virtue of the hybridization and the internuclear distance factors, $^5J_{HH'}$ coupling should be favored in the case of bicyclooctane, if the suggestion of Meinwald and Lewis is correct. If, as is expected, cubane has a measurable five-bond coupling and bicyclooctane does not, the mechanism proposed here would be supported at the expense of that of Meinwald and Lewis. Through-bond coupling such as that proposed by Barfield (5) might be expected to be unimportant. In his study, as well as in that by Karplus (6), the calculations emphasize the necessity for coplanarity of the involved bonds. In the cubane case, two 90° angles are involved. Moreover, the maximum predicted coupling for the four-bond case (5) is about an order of magnitude lower than that predicted in similar fashion for the three-bond case (6), and one might reasonably expect an additional falloff for coupling through five bonds.

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PROPOSITION NO. 5

Abstract

Much is now known about the dependence of the activation energy for hydrogen-atom abstraction reactions on the heat of the abstraction reaction. Experiments are proposed to determine the dependence of the activation energy on the C–H bond dissociation energy for symmetrical thermoneutral processes.

Discussion

In the field of free-radical chemistry, successful and useful correlations of structure and reactivity have been found in the area of abstraction reactions. For a generalized reaction

$$R\cdot + H - X \longrightarrow R - H + X\cdot \qquad + \Delta H \quad , \tag{1}$$

the Evans and Polanyi relationship (1) states that the activation energy, E_{act}, is given by

$$E_{act} = A - B|\Delta H| \tag{2}$$

for exothermic reactions ($\Delta H \leq 0$) and

$$E_{act} = A + (1 - B)|\Delta H| \tag{3}$$

for endothermic reactions, where A and B are constants characteristic of a particular reaction series. The case of $R\cdot$ = methyl has been carefully investigated and it is found that the activation energies for exothermic reactions are closely fit by eq. 4 (1b).

$$\begin{aligned} E_{Me} &= 14.5 - 0.49|\Delta H| \\ &= 0.49[D(C-H) - 74.3] \end{aligned} \qquad (4)$$

The second line follows from the first because $\Delta H = D(C-H) - D(CH_3-H)$. Trotman-Dickenson considers eq. 4 to be of sufficient predictive value to allow the deduction of C–H bond dissociation energies for the cycloalkanes (C_3 to C_7) from measured activation energies for hydrogen abstraction by methyl radicals (1b).

Although eq. 4 applies strictly only for hydrogen abstraction by methyl radicals, the regular decrease in the activation energy envisioned by eq. 4 as the C–H bond dissociation energy of the donor is decreased may be expected for abstraction by other hydrocarbon radicals as well. Useful generalization to other reaction series would thus be possible if but one additional factor were known. The missing link is the dependence of the parameter A of eqs. 2 and 3 on the nature of the radical R· of eq. 1. Equivalently, what is presently unknown is the dependence of the activation energy on the C–H bond dissociation energy for symmetrical thermoneutral abstraction reactions. This quantity is 14.5 kcal/mole for abstraction from methane by methyl radicals (1b). We propose that the activation energies be measured for the analogous processes involving _t_-butyl and cyclohexadienyl radicals:

$$(CH_3)_3C\cdot + (CH_3)_3C^{*}-H \longrightarrow (CH_3)_3C-H + (CH_3)_3C\cdot^{*}$$

A recent scheme advanced by Johnston and Paar predicts a slight lowering of E_{act} for such processes as D(C–H) is decreased (2), perhaps to 13 kcal/mole for t-butyl [D(t-butyl-H) = 91 kcal/mole (1c)] and to 11 kcal/mole for cyclohexadienyl [D(cyclohexadienyl-H) = 70 kcal/mole (3)]. Determination of the actual values would allow a test to be made of the predictive value of Johnston and Paar's scheme and would enable future schemes to be calibrated more broadly and representatively.

Experimentally, the determinations would involve photolytic decomposition of azo compounds, L–N=N–L, where L is labeled t-butyl or labeled cyclohexadienyl, in the gas phase in the presence of the appropriate hydrocarbon, UH, where U is unlabeled t-butyl or cyclohexadienyl. Appropriate reaction products would be collected and analyzed for label content relative to that in the starting azo compound. The idea is that the label content would be diminished to the extent that the exchange reactions depicted above compete with bimolecular consumption of radicals. If rate constants for the latter processes are denoted by k_1 (neglecting isotope effects) and the rate constant for the hydrogen-abstraction process is denoted by k_2, one can show that consideration of loss of label in the reaction products determines the ratio $k_2/k_1^{\frac{1}{2}}$. Bimolecular reaction of t-butyl radicals is known to require no activation energy (4) and bimolecular reaction of cyclohexadienyl radicals occurs at a rate which is within a factor of ten of the rate calculated by collision theory (5), suggesting a minimal or nonexistant activation energy here as well. Thus experiments at several temperatures would yield k_2, as desired.

The labeled azo compounds would be prepared by oxidative coupling of appropriately labeled amines with iodine pentafluoride, as described by Stevens for preparation of 2, 2'-azoisobutane (6). Use of completely deuterated 2, 2'-azoisobutane would allow convenient determination by nmr or mass spectroscopy of the deuterium and hydronium content of the coupling product, hexamethylethane. However, the ratio of disproportionation to coupling is 4.6:1 for t-butyl radicals (7), and existence of a primary isotope effect for disproportionation of d_9-t-butyl radicals could change this ratio appreciably. Thus, yields of d_{18}-, d_9-, and d_0-hexamethylethane would not directly represent the relative amounts of pairwise reaction of the various combinations of labeled and unlabeled t-butyl radicals. It may therefore be preferable to employ a single deuterium label in each t-butyl group. One could partially reduce methylene bromide with tri-n-butyltin deuteride (8), add the Grignard reagent of the resulting d_1-methyl bromide to acetone, and convert the monolabeled t-butyl alcohol to the amine using the Ritter procedure (9), as employed by Barber and Lunt for conversion of 1-methylcyclohexanol to the amine (10). The relative amounts of di-, mono-, and unlabeled hexamethylethane could be inferred by mass spectroscopy.

Monolabeled cyclohexadienyl amine could be prepared starting from 2-bromotoluene. Hydrolysis of the Grignard reagent of this compound with deuterium oxide and oxidation of the resulting toluene would afford ring-labeled benzoic acid. Birch reduction of the acid would afford the labeled 1,4-dihydrobenzoic acid (11), and amination followed by Hofmann degradation would yield the desired cyclohexadienylamine.

Following the reaction of the azo compound, the mixture of isomeric dimers (5), expected to be formed in about 70% yield (3), would be collected by preparative gas chromatography and analyzed by mass spectroscopy. If reaction temperatures as high as 100° should prove to be necessary to effect the desired competition between hydrogen abstraction and dimerization, reaction times would have to be held to less than 100 hours to prevent redissociation of once-formed dimer (12).

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