SYNTHESIS AND THERMAL DECOMPOSITION OF <u>CIS</u>-3,4,5,6-TETRAHYDROPYRIDAZINE-3,4-d_2

Thesis by
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In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

1980

(submitted September 10, 1979)

To Mom and Dad

ACKNOWLEDGEMENTS

Many thanks to Peter Dervan who made working for him both enjoyable and rewarding. Also, thanks to my fellow group members who made lab life pleasant and were always ready with helping hands.

I am eternally (don't hold me to that) grateful to the group of close friends I've had the pleasure of meeting at Caltech (you know who you are) for helping me retain some remnants of reasons and sanity in this asylum.

Certainly no hands were more helpful in a pinch than Debbie Chester's who typed this tenuous tome. Also thanks to the Fluor Corporation for a year of support and to Caltech for the rest.

ABSTRACTS

Chapter I

The stereospecific syntheses of *cis*-tetrahydropyridazine-3,4-d_2 (**6**) and *cis*- and *trans*-cyclobutane-1,2-d_2 are reported. The thermal decomposition of *cis*-tetrahydropyridazine-3,4-d_2 (**6**) (gas phase, 439°) affords 67.1 ± 0.9% *cis*-ethylene-1,2-d_2, 16.1 ± 0.8% *trans*-ethylene-1,2-d_2, 9.4 ± 0.4% *cis*-cyclobutane-1,2-d_2, 7.4 ± 0.4% *trans*-cyclobutane-1,2-d_2. The relative rates of rotation, cleavage, and closure for this 1,2-diazene generated tetramethylene-d_2 are k(cleavage)/k(closure) = 2.2 ± 0.2 and k(rotation)/k(closure = 12 ± 3. An extra stereospecific cleavage component (46%) superimposed on the 1,4-biradical pathway (54%) from the parent tetrahydropyridazine was found, similar to that observed in the 3,4-dimethyl-3,4,5,6-tetrahydropyridazine thermal reactions. Finally, the experimental data for the parent 1,4-biradical, tetramethylene, are compared to calculated values in the literature.

Chapter II

The gas phase pyrolysis of 3,3,4,4-tetramethyldiazetine has been performed in the inlet system of a photoelectron spectrometer. By analysis of the observed internal energy content of the nascent nitrogen and 2,3-dimethyl-2-butene products, estimates on the limits of the amount of reaction exothermicity released to vibration of the nitrogen fragment could be made. It appears that nitrogen acquires very little of the available energy and the implications of this result are discussed in terms of a model which has been proposed for distinguishing concerted and stepwise decomposition of azo compounds.

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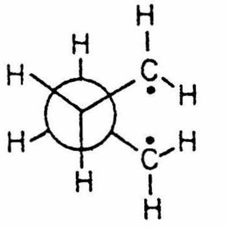
CHAPTER I

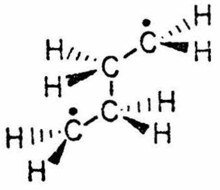
Synthesis and Thermal Decomposition of *cis*-3,4,5,6-Tetrahydropyridazine-3,4-d_2

INTRODUCTION

The only simple 1,4-biradical described by theorists[1] to date is tetramethylene (1). Hoffmann's extended Hückel (EH) calculation for the energy surface between cyclobutane and two molecules of ethylene revealed a rather flat hypersurface.[1b] Segal concluded from an ab initio calculation (SCF at STO-3G level) that there are two well-defined potential energy minima for the gauche and trans conformations of tetramethylene. The barriers ($\Delta H^{\neq}$) to cleavage and closure for gauche-tetramethylene are 3.6 and $\geq$ 2.0 kcal/mol, respectively.[1f] Benson's thermochemical estimates[2] predict similar differences between the heats of formation of the transition states for cleavage and closure from tetramethylene but a deeper well (Figure 1). Despite the fact that substantial experimental work now exists on 1,4-biradical behavior,[3-8] the relative rates of rotation, cleavage, and closure of the parent system are unknown.



1 *gauche*



1 *trans*

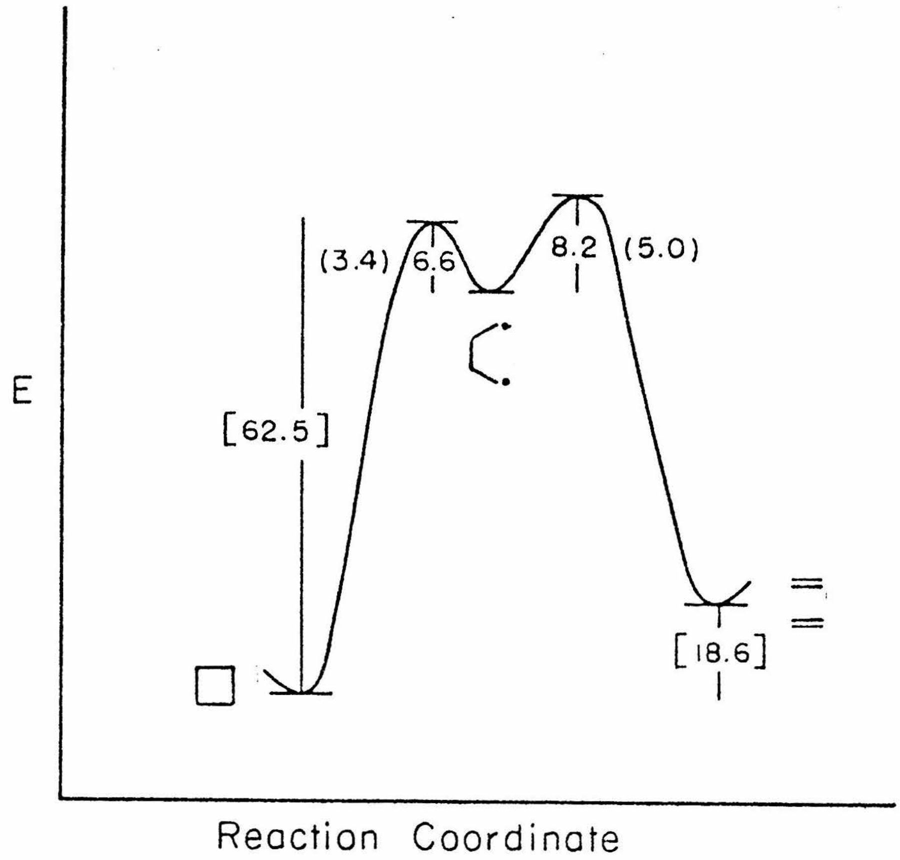
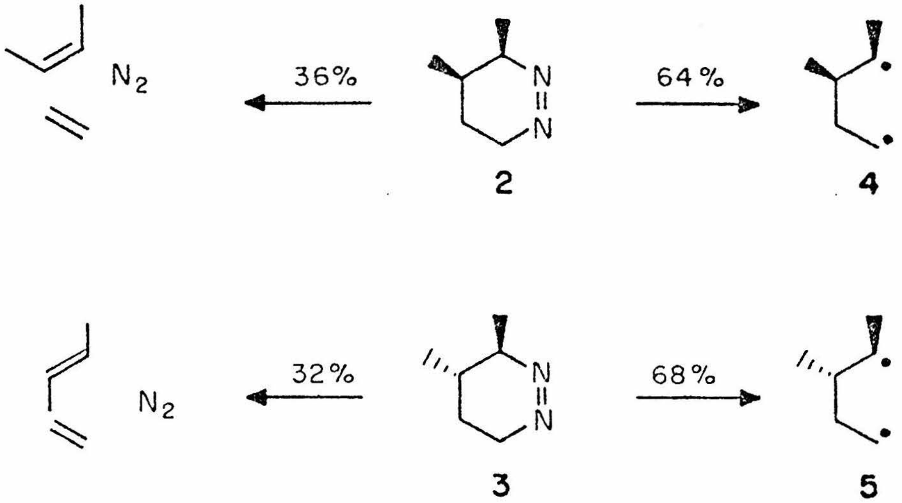


Figure 1. Potential energy profile of cyclobutane to ethylene. Energies are in kcal mol^{-1}. Experimental values (in brackets) are from cyclobutane pyrolysis and heat of formation data. Segal's values are in parentheses, the other values are Benson's estimates.

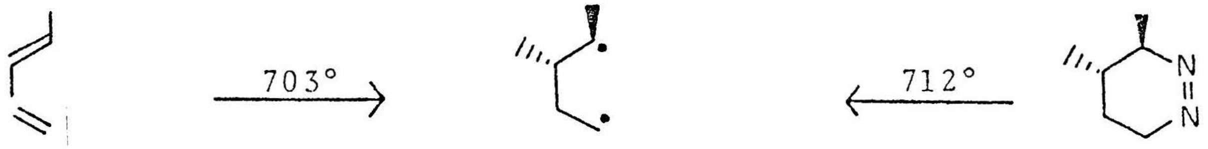
Substituted tetrahydropyridazines have been shown to be excellent sources for the thermal generation of stereospecifically labeled 1,4-biradicals.^{5} Recently, the synthesis and study of the product ratios from the thermal decomposition of *cis*- and *trans*-3,4-dimethyl-3,4,5,6-tetrahydropyridazines (2 and 3) allowed the experimental determination of the relative rates of rotation, cleavage, and closure of two isomeric 1,4-biradicals with secondary radical centers, 3-methyl-1,4-pentanediyl (4 and 5).^{5d,e} These substituted six-membered cyclic 1,2-diazenes were shown to undergo a stereospecific fragmentation reaction to olefin (36-32%) in competition with the generation of a 1,4-biradical intermediate(s) (64-68%) which was *identical in behavior* with the intermediate(s) from the pyrolyses of 1,2-dimethylcyclobutanes (Scheme I).^{5d,e}

Scheme I

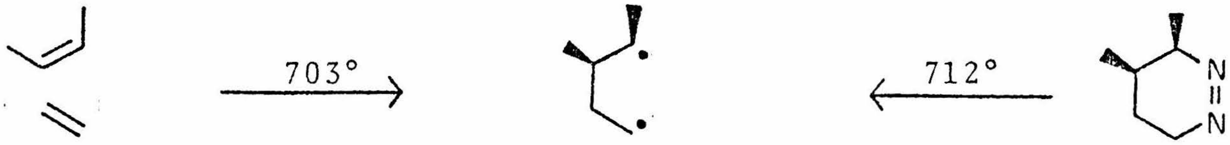


Recently, Scacchi, Richards and Bach studied the thermal cycloaddition of ethylene to cis- and trans-2-butenes (420° at 12 atm).[4c] Their results show that these cycloaddition reactions are the reverse of the decomposition reactions of 1,2-dimethylcyclobutanes. From these experiments, the relative rates of rotation, cleavage, and closure for 3-methyl-1,4-pentanediyl were determined. Agreement of the cycloaddition data with the 1,2-diazene-derived ratio is quite good (Table 1).[5e,9]

Table 1



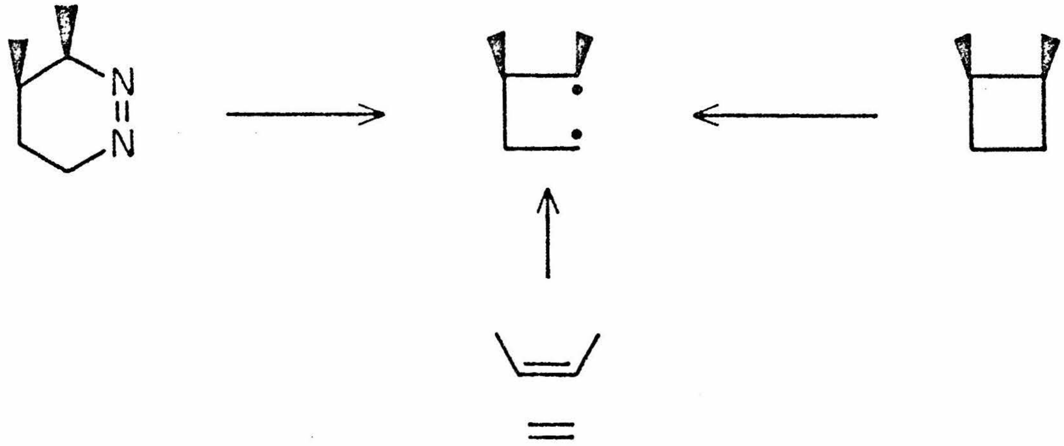
1.5	$\frac{k(\text{cleavage})}{k(\text{closure})}$	1.6
1.4	$\frac{k(\text{closure})}{k(\text{rotation})}$	1.9



1.2	$\frac{k(\text{cleavage})}{k(\text{closure})}$	1.8
0.8	$\frac{k(\text{closure})}{k(\text{rotation})}$	0.7

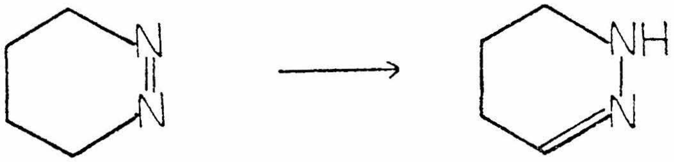
Three different experiments (cyclobutane, 1,2-diazene, 2 + 2 cycloaddition) which characterize the substituted 1,4-biradical, 3-methyl-1,4-pentanediyl are internally consistent (Scheme II). With the establishment of six-membered cyclic 1,2-diazenes as precursors for the thermal generation of 1,4-biradicals we will apply this method to the parent tetramethylene problem to afford a direct comparison of experiment and theory.

Scheme II



This thesis describes (a) the stereospecific synthesis and thermal decomposition in the gas phase (439°) of cis-3,4,5,6-tetrahydropyridazine-3,4-d_2 (6) and (b) the stereospecific syntheses of cis- and trans-cyclobutane-1,2-d_2 (7 and 8).[10] Analyses of the cis/trans stereochemistry in the products from the decomposition of 6 allow an experimental determination of the relative rates of rotation, cleavage, and closure for tetramethylene (1). Moreover, a stereospecific cleavage reaction to ethylene and nitrogen in competition with a 1,4-biradical pathway from the thermal decomposition of 3,4,5,6-tetrahydropyridazine becomes evident.

Before a stereospecific synthesis of cis-3,4,5,6-tetrahydropyridazine-3,4-d_2 could be attempted, a synthesis and thermal decomposition of the unlabeled parent cyclic 1,2-diazene was necessary. We anticipated this 1,2-diazene would suffer the notoriously facile irreversible 1,2-diazene to hydrazone tautomerization associated with 1,2-diazenes that have enolizable hydrogens (in this case four).[5d,e] In the synthesis, purification, and thermal decomposition of the methyl-substituted six-membered cyclic 1,2-diazenes, Uyehara overcame these lability problems by using inert atmosphere and vacuum line techniques in the final stages of the synthetic sequence.[5e] The successful completion of the tetramethylene-d_2 problem then involves the following chronological sequence. (a) Repeat the Uyehara syntheses and thermal decompositions of cis- and trans-



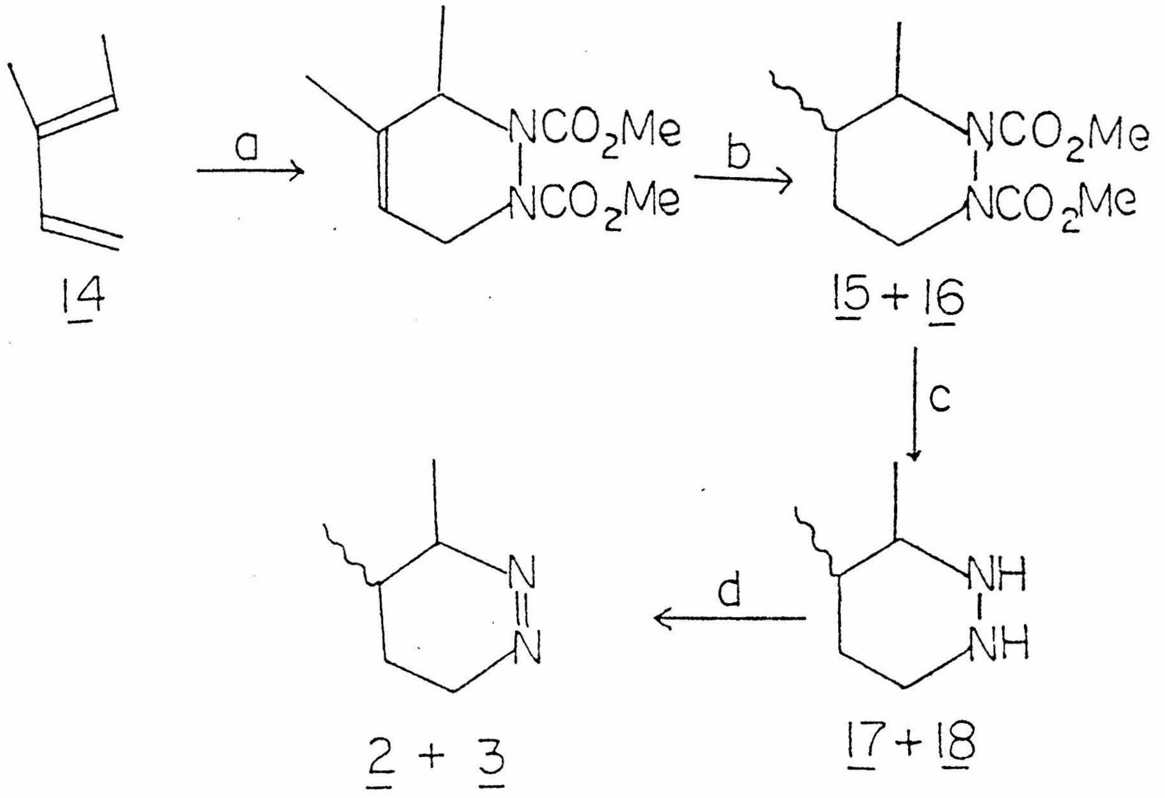
3,4-dimethyl-3,4,5,6-tetrahydropyridazines, compounds known to suffer the irreversible 1,2-diazene to hydrazone rearrangement in the presence of trace acid, base or light. The few percent hydrogen-shift product that was not dissected out by Uyehara will be analyzed and reported. (b) Synthesize the parent 3,4,5,6-tetrahydropyridazine using the same techniques and determine if there is sufficient cyclobutane product in the thermal decomposition for possible infrared analysis when labeled with deuterium. (c) Synthesize by a stereospecific route <u>cis</u>- and <u>trans</u>-cyclobutane-1,2-d_2 and determine if they are distinguishable by infrared analysis. (d) Synthesize by a stereospecific route <u>cis</u>-3,4,5,6-tetrahydropyridazine-3,4-d_2 for the thermal generation of tetramethylene-d_2.

RESULTS AND DISCUSSION

Synthesis and Thermal Decomposition of cis- and trans-3,4-Dimethyl-3,4,5,6-tetrahydropyridazenes (2) and (3).

Synthesis of the diurethanes was accomplished by the Diels-Alder reaction of trans-3-methyl-1,3-pentadiene (14) and dimethylazodicarboxylate, followed by catalytic hydrogenation over platinum yielding a 2:3 mixture of 15 and 16 (Scheme III). Compounds 15 and 16 were separated and purified by preparative VPC. The stereochemistry had been assignmed previously by Uyehara.[5e] Hydrolysis of the diurethanes followed by decarboxylation was carried out under an inert atmosphere (N_2) using thoroughly degassed solvents. The cis- (and trans-)hydrazine products 17 and 18 were distilled on a vacuum line (10^{-4} Torr). Oxidation of the pure hydrazines in benzene-d_6 to the corresponding azo compounds 2 and 3 was accomplished by treatment with oxygen and monitored by NMR. These azo compounds 2 and 3 are extremely sensitive and suffered facile irreversible azo to hydrazone tautomerization in the presence of trace amounts of acid, base, and light.[5e] For pyrolyses, these solutions were injected into an evacuated Pyrex chamber (preheated to 306° or 439°) and the products were collected in a trap at -196°. The product ratios were determined by electronically integrated analytical vapor phase chromatography (VPC) analysis.

Scheme III



(a) $MeO_2CN{=}NCO_2Me$ (b) Pt/H_2 (c) KOH/H_2O, HCl (d) O_2/C_6D_6

The dominant processes that appear to be occurring in these azo derived 1,4-biradicals are rotation, cleavage, and closure (Table 2). Examination of the data reveals that the ratio of trans-2-butene/trans-1,2-dimethylcyclobutane is higher from the trans azo precursor 3 than from the cis-azo precursor 2 (at 439°, 3.0 vs 1.6). Similarly, the ratio of cis-2-butene/cis-1,2-dimethylcyclobutane is higher from the cis-azo precursor 2 than from the trans-azo precursor 3 (at 439°, 4.0 vs 1.8). Thus there is an extra component of stereospecific cleavage of retained

Table 2

		Percent Yields^{a}				
Reactant	Conditions					
cis-2	b	11.2	69.5	4.0	14.6	0.7
	c	11.4	64.4	7.0	16.0	1.2
trans-3	b	69.7	4.3	22.8	2.6	0.6
	c	68.7	5.2	22.5	2.9	0.7

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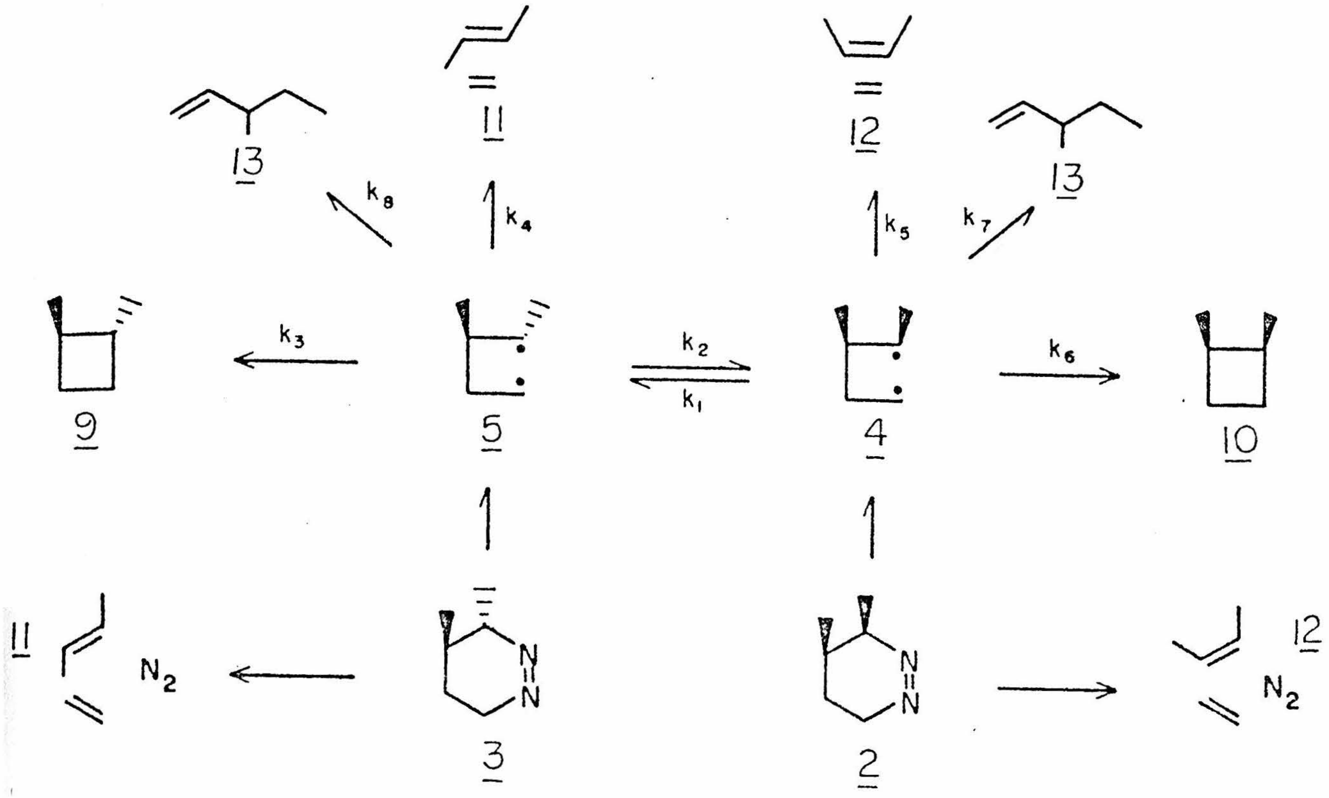
[a] Percent yield based on total hydrocarbon product. Typical absolute yields of hydrocarbon products from 2 and 3 were 50 and 80% at 306° and 439°, respectively. VPC analysis using 20 ft x 1/8 in 10% β,β'-oxydipropionitrile; flame ionizadetector.

[b] Chamber pyrolysis (30s at 306 ± 2°, est. pressure > 25 mm).

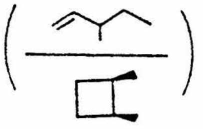
[c] Chamber pyrolysis (5s at 439 ± 2°, est. pressure > 31 mm).

stereochemistry from each azo compound. Consider the following kinetic scheme (Scheme IV). The ratio of k(cleavage)/k(closure) from each biradical (4 and 5) can be obtained directly from the azo decomposition products. Starting from trans azo 3, the ratio of crossover products cis-2-butene/cis-1,2-dimethylcyclobutane is the relative rate of unimolecular decomposition of biradical 4, k_5(cleavage)/k_6(closure) = 1.79. Similarly, starting from cis azo 2, the ratio of crossover products trans-2-butene/trans-1,2-dimethylcyclobutane is equal to k_4(cleavage)/k_3(closure) = 1.63 for biradical 5.

Scheme IV

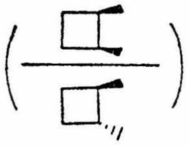


The relative rates of [1,5] hydrogen shifts to closure for each diradical, k_8/k_3 and k_7/k_6, are calculated below.



$$= \frac{k_7(\underline{4}) + k_8(\underline{5})}{k_6(\underline{4})} = \frac{k_7}{k_6} + k_8\left(\frac{(\underline{5})}{k_6(\underline{4})}\right)$$

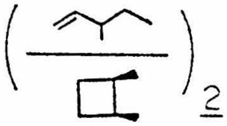
Since



$$= \frac{(\underline{10})}{(\underline{9})} = \frac{k_6(\underline{4})}{k_3(\underline{5})}$$

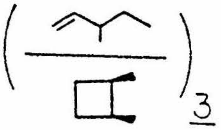
We have $\frac{(\underline{5})}{(\underline{4})} k_6 = \frac{(\underline{9})}{(\underline{10})} k_3$

So from 2



$_{\underline{2}} = \frac{k_7}{k_6} + \frac{k_8}{k_3}\left(\frac{(\underline{9})}{(10)}\right)_{\underline{2}}$

from 3



$_{\underline{3}} = \frac{k_7}{k_6} + \frac{k_8}{k_3}\left(\frac{(\underline{9})}{(\underline{10})}\right)_{\underline{3}}$

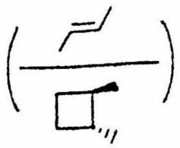
With these two equations containing two unknowns, k_7/k_6 and k_8/k_3, the relative rates of H-shift to closure can be found for 4 and 5.

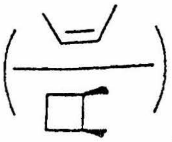
$$\frac{k_7}{k_6} = 0.065$$

$$\frac{k_8}{k_3} = 0.023$$

The k(cleavage)/k(closure) ratios R_1 and R_2, the trans/cis ratios of cyclobutane products R_3 and R_4, and the H-shift/closure ratios k_7/k_6 and k_8/k_3 observed from each azo isomer 2 and 3 will allow a determination of k(closure)/k(rotation) from a simple steady state analysis of the proposed diradical scheme (Scheme IV).

Let R_1 and R_2 be the experimentally determined crossover cleavage/closure ratios.

$R_1 =$  2 $= \frac{k_4}{k_3}$

$R_2 =$  3 $= \frac{k_5}{k_6}$

From trans azo 3 using the steady state assumption d(4)/dt = 0:

$$\frac{d(\underline{4})}{dt} = k_2(\underline{5}) - (k_1 + k_5 + k_6 + k_7)(\underline{4}) = 0$$

$$\frac{(\underline{5})}{(\underline{4})} = \frac{k_1 + k_5 + k_6 + k_7}{k_2}$$

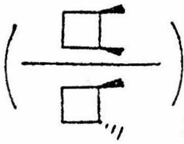
Since

$$\frac{d(\underline{10})}{dt} = k_6(\underline{4})$$

and

$$\frac{d(\underline{9})}{dt} = k_3(\underline{5})$$

then

$R_3 =$  3 $= \frac{k_3(\underline{5})}{k_6(\underline{4})} = \frac{k_3}{k_6}\left(\frac{k_1 + k_5 + k_6 + k_7}{k_2}\right)$

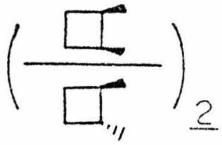
(equation 1) $$R_3 = \frac{k_3}{k_2}\left(\frac{k_1}{k_6} + \frac{k_5}{k_6} + \frac{k_7}{k_6} + 1\right)$$

From cis-azo $\underline{2}$, using the steady-state assumption $d(\underline{5})/dt = 0$

$$\frac{d(\underline{5})}{dt} = k_1(\underline{4}) - (k_3 + k_4 + k_2 + k_8)(\underline{5}) = 0$$

$$\frac{(\underline{4})}{(\underline{5})} = \frac{k_3 + k_4 + k_2 + k_8}{k_1}$$

R_4 =



$$= \frac{k_6}{k_3}\left(\frac{k_3 + k_4 + k_2 + k_8}{k_1}\right)$$

(equation 2) $$R_4 = \frac{k_6}{k_1}\left(\frac{k_4}{k_3} + \frac{k_2}{k_3} + \frac{k_8}{k_3} + 1\right)$$

From experimental data, we have $R_3 = 7.76$, $R_4 = 2.29$, $k_4/k_3 = R_1 = 1.63$ and $k_5/k_6 = R_2 = 1.79$. We also derived that $k_8/k_3 = 0.023$ and $k_7/k_6 = 0.065$. Therefore we can write

(equation 1) $7.76 = k_3/k_2\ (k_1/k_6 + 1.79 + 0.065 + 1)$.

(equation 2) $2.29 = k_6/k_1\ (1.63 + k_2/k_3 + 0.023 + 1)$.

Again, we have two equations with two unknowns. Solving for k_3/k_2 and k_6/k_1, we find that $k_3/k_2 = 1.83$ and $k_6/k_1 = 0.72$. The relative rates of rotation, cleavage, closure and H-shift for biradicals $\underline{5}$ and $\underline{4}$ are listed in Table 3. Therefore, from six experimental ratios from the VPC data of the azo pyrolyses (R_1, R_4, and $\underline{13}/\underline{10}$ from cis-azo $\underline{2}$, and R_2, R_3, and $\underline{13}/\underline{10}$ from trans-azo $\underline{3}$) we could determine the relative rates for all of the processes occurring from the two biradicals.

Table 3

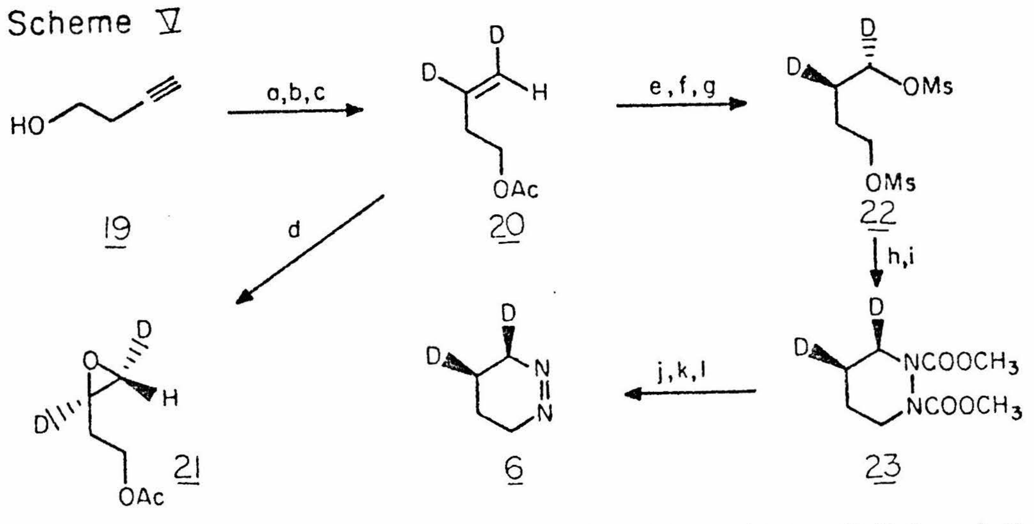
The Relative Rates of Rotation, Cleavage, Closure and H-Shift for 5 and 4 at 439°

5		4
$\frac{k_4}{k_3} = 1.63$	$\frac{k(\text{cleavage})}{k(\text{closure})}$	$\frac{k_1}{k_6} = 1.79$
$\frac{k_2}{k_3} = 0.546$	$\frac{k(\text{rotation})}{k(\text{closure})}$	$\frac{k_1}{k_6} = 1.39$
$\frac{k_8}{k_3} = 0.023$	$\frac{k(\text{H-shift})}{k(\text{closure})}$	$\frac{k_7}{k_6} = 0.065$

Synthesis and Thermal Decomposition of cis-3,4,5,6-Tetrahydropyridazine-3,4-d_2 (6).

The stereospecific synthesis of cis-3,4,5,6-tetrahydropyridazine-3,4-d_2 (6) was accomplished as shown in Scheme V.

Scheme V



a) CH_3COCl b) $(C_6H_{10}D)_2BD$ c) CH_3COOD d) mCPBA e) BH_3 f) H_2O_2 g) MsCl
h) $(HNCOOCH_3)_2/NaH$ i) NaH j) $KOH/H_2O/N_2$ k) HCl/N_2 l) O_2/C_6D_6

Successive treatment of 3-butyn-1-ol (**19**) with acetyl chloride, dicyclohexylborane-d_1, and acetic acid-O-d afforded *cis*-3-buten-1-yl-3,4-d_2 acetate (**20**). Conversion of this *cis*-3,4-d_2 alkene (**20**) to the corresponding epoxide **21** allowed NMR analysis of the deuterium content of each olefinic position and confirmed the *cis*-3,4-d_2 assignment of **20** (see Experimental Section). Hydroboration of *cis*-1-butenyl-3,4-d_2 acetate (**20**), oxidative work-up, and reaction with methanesulfonyl chloride afforded *threo*-1,4-butanediyl-1,2-d_2 dimethanesulfonate (**22**). Reaction of **22** with dimethyl hydrazine-1,2-dicarboxylate and sodium hydride afforded dimethyl *cis*-tetrahydropyridazine-1,2-dicarboxylate-3,4-d_2 (**23**) (93% d_2, 7% d_1).[11] Hydrolysis of the diurethane **23**, followed by decarboxylation, was carried out under an inert atmosphere (N_2) using thoroughly degassed solvents. The *cis*-hydrazine-3,4-d_2 product **24** was distilled on a vacuum line (10^{-4} Torr). Oxidation of the pure hydrazine **24** in benezene-d_6 to the corresponding *cis*-3,4-d_2 azo compound **6** was accomplished by treatment with oxygen and monitored by NMR. This 3,4,5,6-tetrahydropyridazine is an extremely sensitive compound and suffers facile irreversible1,2-diazene to hydrazone tautomerization in the presence of trace amounts of acid and base. For pyrolyses, this solution was injected into an evacuated Pyrex chamber (preheated to 439°) and the products were collected in a trap at -196°. The ratio of the two ethylenes/cyclobutane was 83.2/16.8 from analytical VPC analysis (Table 4). These products were separated by preparative VPC for infrared analyses of their respective *cis*/*trans*-d_2 ratios.[12]

Table 4

Analysis of Ethylene/Cyclobutane Ratios from

The Pyrolysis of 6

Reactant	Conditions	Percent Yields[a]	
		2 ethylenes	cyclobutane
6-d_2	b	83.2 ± 0.5	16.8 ± 0.5
6-d_0	b	84.4 ± 0.5	15.6 ± 0.5
6-d_0	c	84.6 ± 1.0	15.4 ± 1.0

[a] Percent yield is the corrected ratio of cleavage pathway (two moles of ethylene) to closure pathway (one mole of cyclobutane). Correction for the FID response factors for ethylene to cyclobutane, in addition to the molecular weight difference was 1.07 ± 0.02:1.00. Ethylene and cyclobutane accounted for 99.2% of the volatile hydrocarbon yield. *Ca.* 0.4% of propylene and 0.4% of 1-butene were found by VPC analysis (10' x 1/8" SE-30; flame ionization detector). Errors are standard deviations for three pyrolyses.

[b] Chamber pyrolysis (5s at 439 ± 5°, est. pressure 25 mm).

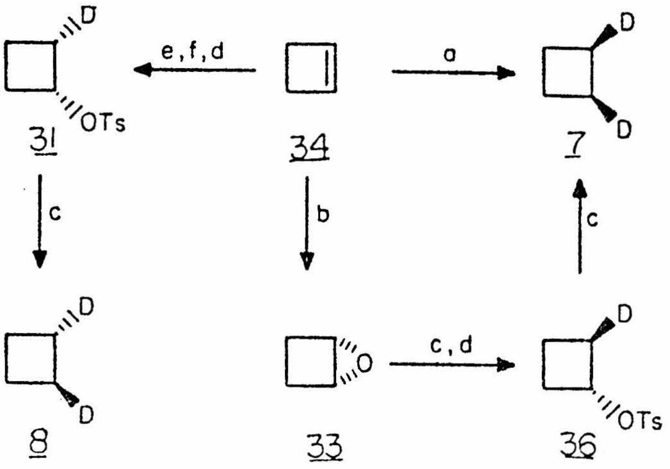
[c] Chamber pyrolysis (30s at 306 ± 5°, est. pressure 17 mm).

Dimethyl-3,4,5,6-tetrahydropyridazine-1,2-dicarboxylate (23-d_0) was synthesized by the hydrogenation of the product from the Diels-Alder reaction between dimethylazodicarboxylate and 1,3-butadiene. The diurethane was converted to the azo compound as described for the deuterated analogue. Pyrolyses and VPC analyses were also carried out in the same manner. The ethylene/cyclobutane ratio was not only similar to that of cis-3,4,5,6-tetrahydropyridazine-3,4-d_2 at 439°, but was relatively unchanged at 306° (Table 2). This compound was synthesized before 6 to see if there was enough cyclobutane produced to allow an analysis of 7 and 8 if 6 were pyrolyzed.

Syntheses and Analysis of cis- and trans-Cyclobutane-1,2-d_2 (7 and 8).

The syntheses of cis- and trans-cyclobutane-1,2-d_2 (7 and 8) are shown in Scheme VI. Treatment of cyclobutene with diimide-d_2 afforded cis-cyclobutane-1,2-d_2 (7) (> 98% cis). An alternate stereospecific route involved successive treatment of cyclobutene with m-chloroperbenzoic acid, lithium triethylborodeuteride, tosyl chloride, and lithium triethylborodeuteride (> 98% cis). Similarly, successive treatment of cyclobutene with borane-d_3, hydrogen peroxide and base, tosyl chloride, and lithium triethylborodeuteride afforded trans-cyclobutane-1,2-d_2 (8) (> 98% trans).

Scheme VI



31 34 7 8 33 36

a) N_2D_2 b) mCPBA c) $LiB(C_2H_5)_3D$ d) TsCl
e) BD_3 f) H_2O_2/OH^-

The ratio of cis/trans-cyclobutane-1,2-d_2 products from the pyrolysis of 6 was determined by measuring the relative ratio of the 1307 cm^{-1} (cis-1,2-d_2) and 1294 cm^{-1} (trans-1,2-d_2) bands in the infrared[12] and comparing these with those of authentic mixtures. The cis-tetrahydropyridazine-3,4-d_2 (6) contains 93% d_2 and 7% d_1 from mass spectral analysis. Since cyclobutane-d_1 has a band at 1307 cm^{-1}, calibration mixtures contained 93% cis,trans-1,2-d_2 and 7% cyclobutane-d_1. The observed cis/trans-cyclobutane-1,2-d_2 ratio from the pyrolysis of 6 obtained by comparison with authentic mixtures is 1.27 ± 0.06 which corresponds to a 56/44 ratio (Table 5).

Table 5

Analysis of Cyclobutane-1,2-d_2 Products from the Pyrolysis of <u>6</u>

cis/*trans*-cyclobutane-1,2-d_2[a]	Infrared peak height ratios ($1307\ cm^{-1}/1294\ cm^{-1}$)
1.22[b]	1.47
1.22	1.34
1.22	1.55
1.01	1.18
1.01	1.25
1.01	1.30
0.83	1.01
0.83	1.06
0.83	1.10
pyrolysis of <u>6</u>[c]	1.51 ± 0.06[d]

---

[a] Authentic mixtures contain 92.5 ± 1.0% cyclobutane-d_2 and 7.5 ± 1% cyclobutane-d_1 (from ICR). The *cis* and *trans* cyclobutane-1,2-d_2 authentic compounds are each > 98% stereochemically pure (by IR analysis).

[b] These ratios are determined by a MKS pressure gauge. The errors for the three mixtures due to pressure gauge accuracy are 1.22 ± 0.01, 1.01 ± 0.02, and 0.83 ± 0.04.

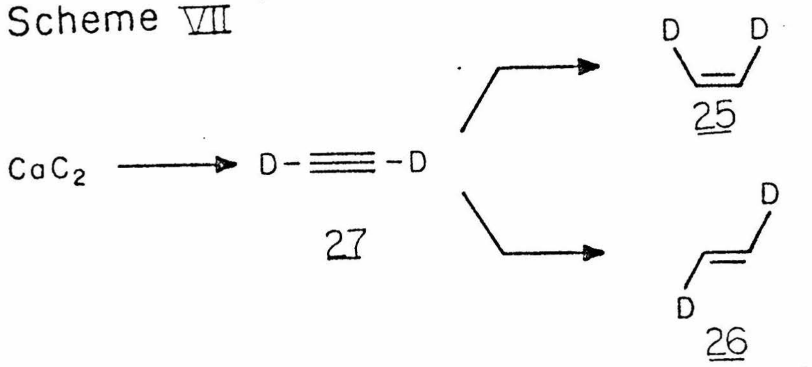
[c] Chamber pyrolysis (5s at 439 ± 5° est. pressure 300 mm) combination of six injections. Contains (92.5%-d_2 and 7.5%-d_1 by ICR.

[d] Peak ratio is the average of four spectra. The error is the standard deviation.

Synthesis and Analysis of *cis*- and *trans*-Ethylene-1,2-d_2 (25 and 26).

The syntheses of *cis*- and *trans*-ethylene-1,2-d_2 (25 and 26) were carried out using the methods of Nicholas and Carroll (Scheme VII).[13]

Scheme VII



The *cis*/*trans*-ethylene-1,2-d_2 ratios from the pyrolysis of 6 can be obtained by measuring the 842 cm^{-1} (*cis*-1,2-d_2) and the 724 cm^{-1} (*trans*-1,2-d_2) bands in the infrared[12] and comparing these with those of the authentic mixture (Table 6).

From the pyrolysis of 6 the observed infrared peak height ratio (842/724 cm^{-1}) is 4.9 ± 0.4. By comparison with the authentic mixtures we find the *cis*/*trans*-ethylene-1,2-d_2 ratio is 4.15. Using the measured relative extinction coefficients of the 842 cm^{-1} and 724 cm^{-1} peaks, the *cis*/*trans*-ethylene-1,2-d_2 ratio from the pyrolysis of 6 can be obtained directly, 4.9/1.18 = 4.15 which corresponds to an 80.6/19.4 *cis*/*trans* ratio.

Table 6

Analysis of Ethylene-1,2-d_2 Products from the Pyrolysis of 6

cis/trans-ethylene-1,2-d_2	IR Peak Height Ratio[a] (842 cm^{-1}/724 cm^{-1})
15.7[b]	13.2
4.88[b]	5.7
3.76[b]	4.5
2.85[b]	3.7
1:1[c]	1.18
pyrolysis of 6[d]	4.9 ± 0.4[e]

[a] Infrared Mode of Operation: Manual slit control mode (see Experimental Section).

[b] These authentic mixture ratios are determined by a MKS pressure gauge. The error is less than 1%. Stereochemical purity of each isomer is > 99%. The isotopic purities were determined by ICR spectrometry to ± 1%.

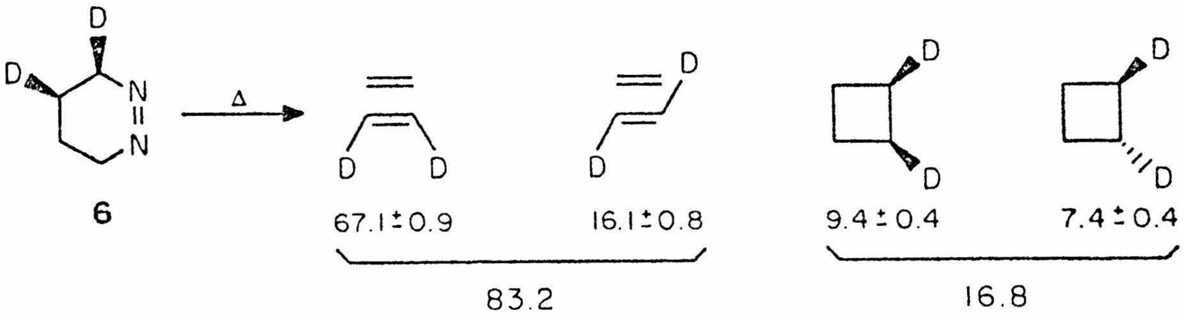
[c] The relative extinction coefficient of the 842 cm^{-1} (cis-d_2) and 724 cm^{-1} (trans-d_2) bands was determined by comparing the relative extinction coefficient of the 842 cm^{-1} and 806 cm^{-1} (ethylene-d_1) bands in isomerically pure cis-ethylene-d_2 contaminated with ethylene-d_1 to the relative extinction coefficient of the 724 cm^{-1} and 806 cm^{-1} bands in isomerically pure trans-ethylene-d_2 contaminated with ethylene-d_1. The ratio of d_2 to d_1 compound in each sample was determined by ICR spectroscopy.

[d] Chamber pyrolysis (5s at 439 ± 5°, est. pressure 300 mm).

[e] Standard deviation of four measurements from two pyrolyses.

A summary of the stereochemical results from the thermal decomposition of *cis*-3,4,5,6-tetrahydropyridazine-3,4-d_2 (**6**) is shown in Scheme VIII (see Experimental Section for a derivation of these values and the standard deviations).

Scheme VIII

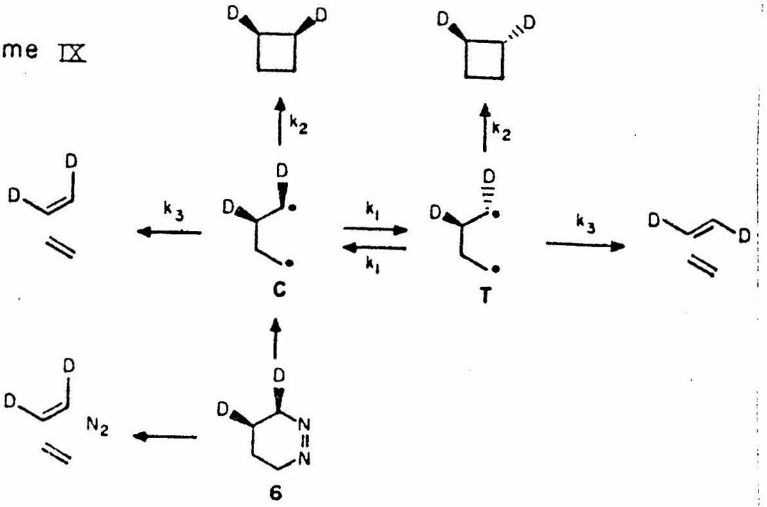


Kinetic Scheme

Examination of the data reveals that the ratio of *cis*-ethylene-1,2-d_2/*cis*-cyclobutane-1,2-d_2 is higher than the ratio of *trans*-ethylene-1,2-d_2/*trans*-cyclobutane-1,2-d_2. Therefore, there exists an *extra component of stereospecific cleavage* of retained stereochemistry from the 1,2-diazene **6** thermal decomposition.

By analogy to the previously described decomposition pathways for *cis* and *trans*-3,4-dimethyl-3,4,5,6-tetrahydropyridazines[5d,e] consider the kinetic Scheme IX.

Scheme IX



The ratio of k(closure)/k(cleavage) can be obtained directly. From 6 the ratio of crossover products, trans-cyclobutane-1,2-d_2:trans-ethylene-1,2-d_2 is equal to the ratio of the rates for closure and cleavage in the unimolecular decomposition of biradical T. From Scheme VIII trans-cyclobutane-1,2-d_2/trans-ethylene-1,2-d_2 = 7.4/16.1 = 0.46 = k_2(closure)/k_3(cleavage). This k_2(closure)/k_3(cleavage) ratio (R_1) and the ratio of cis/trans-cyclobutane-1,2-d_2 (R_2) allow a determination of the k_2(closure)/k_1(rotation) ratio from a simple steady-state analysis of the proposed diradical scheme. Using steady-state approximations

$$\frac{d(T)}{dt} = k_1(C) - (k_2 + k_3 + k_1)(T) = 0$$

$$\frac{(C)}{(T)} = \frac{k_2 + k_3 + k_1}{k_1}$$

$$R_2 = \frac{k_2(C)}{k_2(T)} = \frac{k_2}{k_1} + \frac{k_3}{k_1} + 1$$

$$R_2 \cdot \frac{k_2}{k_3} = \frac{k_2}{k_1} \cdot \frac{k_2}{k_3} + \frac{k_3}{k_1} \cdot \frac{k_2}{k_3} + \frac{k_2}{k_3}$$

$$R_2 \cdot R_1 = \frac{k_2}{k_1} R_1 + \frac{k_2}{k_1} + R_1$$

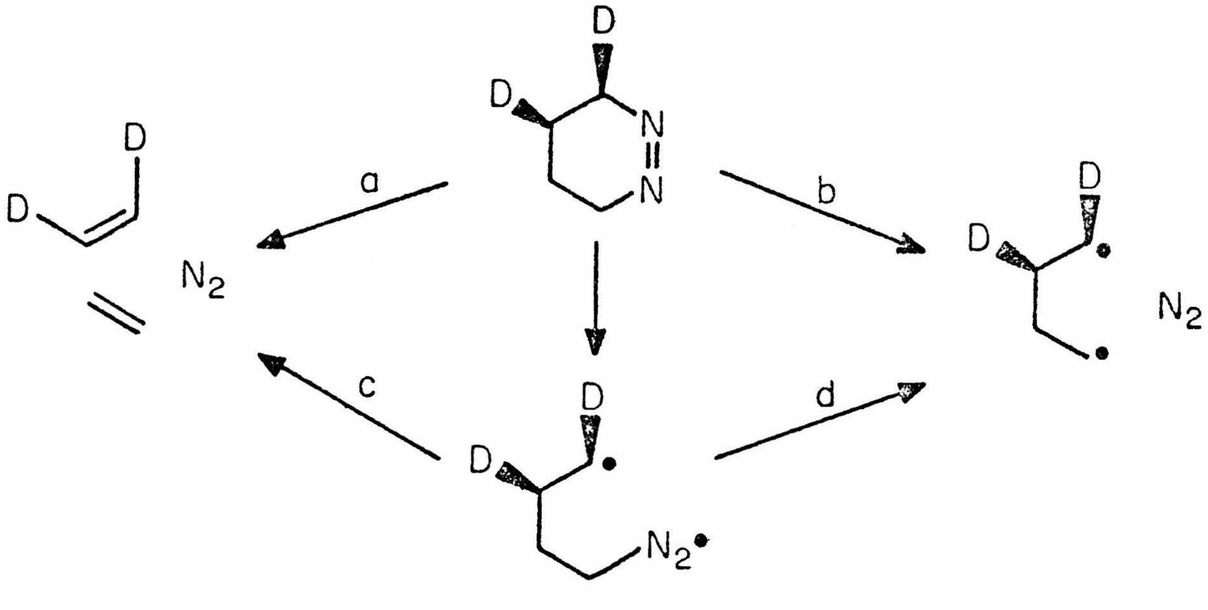
$$\frac{k_2}{k_1} = \frac{(R_2R_1 - R_1)}{(R_1 + 1)}$$

From Scheme VIII, $R_1 = k_2/k_3 = 0.46$ and R_2 = cis/trans-cyclobutane-1,2-d_2 = 1.27. Substituting R_1 and R_2 from the pyrolysis data, we find k_2(closure)/k_1(rotation) = 0.085. The relative rates of rotation, cleavage, and closure for tetramethylene-d_2 are k_3(cleavage)/k_2(closure) = 2.2 ± 0.2 and k_1(rotation)/k_2(closure) = 12 ± 3.

The amount of stereospecific fragmentation to ethylene and nitrogen from tetrahydropyridazine can be calculated. From Scheme VIII, the experimental ratio of cis-ethylene-1,2-d_2/cis-cyclobutane-1,2-d_2 is 67.1:9.4. From k_3/k_2, the amount of cis-ethylene-1,2-d_2 expected from 1,4-biradical C should be 2.2 times the cis-cyclobutane-1,2-d_2 observed (9.4 x 2.2 = 20.7%). Therefore the extra stereospecific component of cis-ethylene-1,2-d_2 is 67.0 - 20.7 = 46.3%. This established another example of an extra cleavage component superimposed on the 1,4-biradical pathway from a six-membered cyclic 1,2-diazene decomposition.[5d,e] This may be the result of a 2+2+2 cycloreversion pathway[14] (path a) which is nearly equienergetic with a 1,4-biradical pathway (path b) or the decomposition of a diazenyl biradical that does not lose stereochemical integrity (path c and d) (Scheme X) or some combination of all four.

The critical assumption of our analysis is that if the decomposition of 6 does proceed by a stepwise decomposition to an intermediate diazenyl biradical, then this diazenyl biradical does not lose stereochemical integrity before decomposition to tetramethylene. This assumption is valid in the substituted 1,2-diazene fragmentation study since identity with the intermediate from the pyrolysis of 1,2-dimethylcyclobutane was shown.[5d,e] However, it is not known in this case, and we must await an independent check of identity from another precursor, perhaps a study of cyclobutane-d_4 thermal reactions.[15]

Scheme X



By estimating the structures of the transition states for the cleavage and closure of tetramethylene, Benson used thermochemical estimates[2] to predict entropies of activation for the two processes. Combining these values with the theoretical activation energies from the work of Benson[2] and Segal,[1f] the ratio of cleavage and closure rates can be calculated and the relative rates can be compared to the experimental results presented here (Table 7). From the k(cleavage)/k(closure) ratio reported here (2.2) one calculates that E_a(cleavage) > E_a(closure) by 1.4 kcal mol^{-1} at 712°K assuming Benson's estimated frequency factors.

Table 7

Thermochemical and Kinetic Data for the Reactions

	Closure	Cleavage
log $A^{\neq}$ (sec^{-1})[a]	12.30	13.07
E_a, kcal mol^{-1} (Benson)	6.6	8.2
E_a, kcal mol^{-1} (Segal)	> 3.4	5.0
rel. rates (Benson)[b]	1	1.9
rel. rates (Segal)[b]	1	$\geq$ 1.9
rel. rates (experimental)[c]	1	2.2 ± 0.2

[a] Benson's thermochemical estimates.[2]

[b] $k = Ae^{-E_a/RT}$ $T = 712°\text{K}$

[c] This paper.

The depth of the energy well for tetramethylene is still not known. Experimental determination of this value requires the measurement of the absolute rate of one of the processes involved, i.e., rotation, cleavage, or closure. Experimental measurements of the activation energy for rotation of primary radicals have been reported.[17] The values of the activation energy of rotation range from 0.4 to 3.1 kcal mol^{-1} depending on the method of analysis. When reliable Arrhenius parameters for rotational barriers in radicals are available, estimates of the tetramethylene well depth can be made. Using presently available values, the energy well parameters are estimated (see Table 8).[18]

Table 8

Tetramethylene Energy Well Parameters

	Cleavage	Closure	Rotation
log A (sec^{-1})[a]	13.1	12.3	12.3
E_a, kcal mol^{-1}[b]	5.3-8.0	3.9-6.6	0.4-3.1

[a] Benson's values.[18]

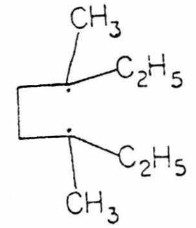
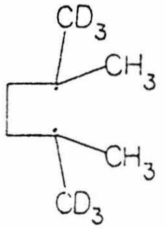
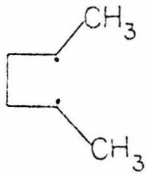
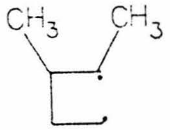
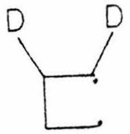
[b] Using the rotation barriers of 0.4 and 3.1, the E_a's for cleavage and closure are calculated using k(rotation)/k(closure) = 12 and k(cleavage)/k(closure) = 2.2

Factors affecting relative rotational propensities[19] of variously substituted 1,4-biradicals have been of interest, but complicated by the scarcity of examples of biradicals generated under similar conditions. A comparison of primary, secondary, and tertiary-substituted presumed 1,4-biradicals generated from 1,2-diazenes and cyclobutanes is presented in Table 9. If the closure rate is assumed to be constant, a significant slowing of the rotation rate is observed as one proceeds from primary to tertiary radical centers. If steric deceleration of the closure rate does occur, the rotational rate differences are even greater. One finds that as substitution at the radical center increases (1° → 2° → 3°) the rotation rate in 1,4-biradicals decreases more than two orders of magnitude.

The $k_{rotation}/k_{closure}$ values for the first five entries in Table 9 had to be estimated from retention/inversion values originally reported. For the first two examples, Bartlett and Porter gave $k_{retention}/k_{isomerization}$ values > 49/1 for both meso and dl-3,6-dimethyl-3,6-diethyltetrahydropyridazine.[5a] In addition, the reaction gave an equal amount of olefin products (cleavage) and cyclobutane products (closure). Using the same kinetic scheme that was derived for this paper (since meso and dl radicals gave the same results), we have $k_{rotation}/k_{closure} = (R_1 + 1)/(R_2R_1 - R_1) = (1/R_2 - 1)) + 1/(R_1(R_2 - 1))$. $R_1 = k_{closure}/k_{cleavage} = 1$. R_2 = cis/

Table 9

Comparison of the Effect of Substitution on k(rotation)/k(closure) for 1,4-biradicals.

		k(rotation)/k(closure)		Conditions	Ref.
	3°	meso	< 0.02	148/soln	5a
		dl	< 0.02	148/soln	
	3°	dl	< 0.05	425/gas	3e
	2°	meso	∿ 1.9	439/gas	5e
		dl	∿ 1.9	439/gas	
	2°	cis	1.4	439/gas	5e
		trans	0.53	439/gas	
	1°	cis	12	439/gas	This work

trans cyclobutane > 49. Therefore, $k_{rotation}/k_{closure} <$ 0.04. (Note that if there is any direct fragmentation component, R_1 will increase. At the limiting value of 50% direct fragmentation (since 50% closure product was observed) $R_1 = \infty$ or $k_{rotation}/k_{closure} = 0.02$.) On a per radical site basis, $k_{rotation}/k_{closure} \leq 0.04/2 = 0.02$.

The third entry in the Table is from the decomposition of trans-1,1,2,2-tetramethylcyclobutane-d_6 by Berson, Tompkins, and Jones.[3e] These workers found that the ratio of decomposition (olefin products) to isomerization (cis-cyclobutane) was $\geq$ 22/1. Using $k_{closure}/k_{cleavage} = 1$, since this is the minimum value found for the similar biradical generated by Bartlett and Porter and results in a maximum value for $k_{rotation}/k_{closure}$, we have $R_1 = 1$. Because olefin/cis-cyclobutane = 22 and total cyclobutane/olefin = 1, we have (cis-cyclobutane + trans-cyclobutane)/olefin = 1 or (trans-cyclobutane + 1)/22 = 1. Therefore, trans-cyclobutane/cis-cyclobutane = 21/1 = R_2. Substituting into $(R_1 + 1)/(R_2R_1 - R_1)$, $k_{rotation}/k_{closure} \leq 0.1$. Since there are two substituted radical sites, $k_{rotation}/k_{closure}$ (per site) ≤ 0.05.

The fourth and fifth entries are from the work of Dervan and Uyehara.[5d,e] It was found that the ratio of cis/trans-1,2-dimethylcyclobutane from the pyrolysis of cis-3,6-dimethyl-3,4,5,6-tetrahydropyridazine was 1.7. The retention/isomerization ratio was also 1.7 starting from the corresponding trans compound. Therefore, the same kinetic analysis can be applied with R_2 = 1.7 and R_1 = ca. 0.59 (R_1 is estimated from the closure/cleavage values obtained for 3-methyl-1,4-pentanediyl). We obtain $k_{rotation}/k_{closure} = 3.8$. On a per rotating radical site basis, $k_{rotation}/k_{closure} = 1.9$. The $k_{rotation}/k_{closure}$ values for the last three entries in Table 9 are obtained analytically from experimental results.

SUMMARY

In summary, from the thermal decomposition of cis-3,4,5,6-tetrahydropyridazine-3,4-d_2 we have measured the relative rates of rotation, cleavage, and closure for tetramethylene-d_2 (k(cleavage)/k(closure) = 2.2 ± 0.2 and k(rotation)/k(closure) = 12 ± 3) and separated a direct cleavage component (46%) in the parent six-membered cyclic-1,2-diazene decomposition. What is needed on both the experimental and theoretical level is more accurate information on the Arrhenius parameters for rotation in both radicals and biradicals. In addition, with regard to the work presented here, a comparison of the relative rates of rotation, cleavage, and closure for tetramethylene from another precursor, eg., cyclobutane-d_4, will be of interest

EXPERIMENTAL SECTION (Part I)

Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan. Infrared spectra (IR) were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Associates A-60A and are uncalibrated. Chemical shifts are given as parts per million (ppm) downfield from Me_4Si in δ units and coupling constants in cycles per second (Hz). Nuclear magnetic resonance data are reported in the order: chemical shift; multiplicity, s = singlet, d = doublet, t = triplet, m = multiplet; number of protons; coupling constants; assignment. Electronic spectra were recorded on a Cary Model 14 spectrophotometer.

For analytical vapor-phase chromatography (VPC), a Hewlett-Packard 5700A Gas Chromatograph, equipped with flame ionization detector and nitrogen carrier gas, was used. The 0.125 in. packed stainless steel columns used in this instrument are listed in Table 10. Quantitative VPC analysis was accomplished using a Hewlett-Packard 3370A electronic digital integrator. For preparative VPC, a Varian Aerograph Model 920 instrument, equipped with thermal conductivity detector and helium carrier gas was used. The 0.375 in. packed aluminum columns used in this instrument are listed in Table 10.

Most reagent-grade chemicals were used without further purification. Diglyme and tetrahydrofuran were distilled from lithium aluminum hydride, and pyridine from barium oxide.

Preparation of a mixture of 15 and 16.

A solution of 10g (0.12 mole) of trans-3-methyl-1,3-pentadiene and 14.6g (0.10 mole) of azodicarboxylate in 80 ml of ether was stirred at room temperature for 6 hr. The solution was concentrated and distilled affording 22g (0.096 mole) of dimethyl-3,4-dimethyl-3,6-dihydropyridazine-1,2-dicarboxylate (96%) bp 110-112° (0.7 mm). Catalytic hydrogenation of the adduct over platinum yielded 20g (95%) of a 2:3 mixture of 16 and 15: bp 80-92° (0.18 mm), which were separated by preparative VPC (FFAP, 205°, rel. retention times, trans-16 = 1.0 and cis-15 = 1.14). This was a more convenient preparation than the stereospecific route which was necessary for isomeric identification.[5e]

15 IR ($CHCl_3$) 1700 (C=O); NMR ($CDCl_3$) δ 0.8-2.0 (m, 9), 0.86 (d, J = 6.2Hz), 1.06 (d, J = 6.8Hz), 2.6-3.3 (m, 1), 3.75 (s, 1), 3.80 (s, 5), 4.1-4.5 (m, 2).

Anal. Calcd. for $C_{10}H_{18}N_2O_4$: C, 52.16; H, 7.88;

N, 12.16. Found: C, 52.10; H, 7.91; N, 12.01.

16 IR ($CHCl_3$) 1698 (C=O); NMR ($CDCl_3$) δ 0.9-2.2 (m, 9), 1.06 (d, J = 6.3Hz), 1.23 (d, J = 6.8Hz), 2.9-4.4 (m, 9), 3.72 (s), 3.76 (s).

Anal. Calcd. for $C_{10}H_{18}N_2O_4$: C, 52.16; H, 7.88; N, 12.16. Found: C, 52.08; H, 8.01; N, 12.16.

Preparation of cis- and trans-3,4-dimethylhexahydropyridazines, 17 and 18.

A general procedure for hydrolysis of each isomerically pure diurethane is as follows:[5e]

0.5g (2 mmol) of the dimethyl-3,4-dimethyltetrahydropyridazine-1,2-dicarboxylate was added to a solution of 1g (18 mmol) of potassium hydroxide in 10 ml of degassed water. The mixture was allowed to reflux with vigorous stirring under a nitrogen atmosphere for 24 hr. This was cooled to 0°, 4 ml of degassed 6N HCl was added via syringe and the reaction mixture was allowed to stir for 0.5 hr. The reaction mixture was made basic with degassed aqueous saturated potassium carbonate and extracted three times with 25 ml portions of ether, freshly distilled under a nitrogen atmosphere and delivered via a double-ended needle. Each extract was transferred via a double-ended needle to a pressure equalizing funnel, containing $MgSO_4$ in a small filter thimble, attached to the top of a distillation head under a slow stream of nitrogen. After the ether solvent was removed by distillation, the remaining oil was distilled on a vacuum line (10^{-4} Torr). The clear colorless hydrazo distillate was distilled into an NMR tube on the vacuum line and diluted with 0.4-0.5 ml of degassed benzene-d_6, which had been purified by preparative VPC (β,β ODP). The NMR tube was sealed and removed.

cis-3,4-dimethylhexahydropyridazine, *17*.

NMR (C_6D_6) δ 0.7-1.8 (m, 9), 0.76 (d, J = 6.6Hz), 0.83 (d, J = 6.8Hz), 2.8-3.3 (m, 5).

trans-3,4-dimethylhexahydropyridazine, *18*.

NMR (C_6D_6) δ 0.6-1.6 (m, 9), 0.85 (d, J = 6.5Hz), 1.8-2.2 (m, 1), 2.5-3.0 (m, 4).

Preparation of *cis*- and *trans*-3,4-dimethyl-3,4,5,6-tetrahydropyridazines, *2* and *3*.

In general, for oxidation, a solution of each dimethylhexahydropyridazine in benzene-d_6 was allowed to stand in the dark under a positive pressure of oxygen (Matheson Gas Products) for several hours. The oxidation reaction was monitored by NMR.

cis-3,4-Dimethyl-3,4,5,6-tetrahydropyridazine (**2**).

The oxidation of *cis*-3,4-hydrazo compound **17** to *cis*-3,4-azo compound **2** was complete in 25 hr affording a 3:1 mixture of *cis*-3,4-dimethyl-3,4,5,6-tetrahydropyridazine (**2**) and the corresponding hydrazone, *cis*-3,4-dimethyl-2,3,4,5-tetrahydropyridazine (**28**). Azo **2**: NMR (C_6D_6): δ 0.47 (d, 3, J = 6.8Hz), 0.65-1.8 (m, 6), 1.44 (d, J = 7Hz), 2.9-3.6 (m, 3). Hydrazone **28** was purified by preparative VPC (Pennwalt, 180°). NMR (C_6D_6) δ 0.5-3.1 (m, 10), 0.61 (d, J = 6.8Hz), 0.75 (d, J = 6.8Hz), 6.65 (m, 1).

trans-3,4-Dimethyl-3,4,5,6-tetrahydropyridazine (**3**).

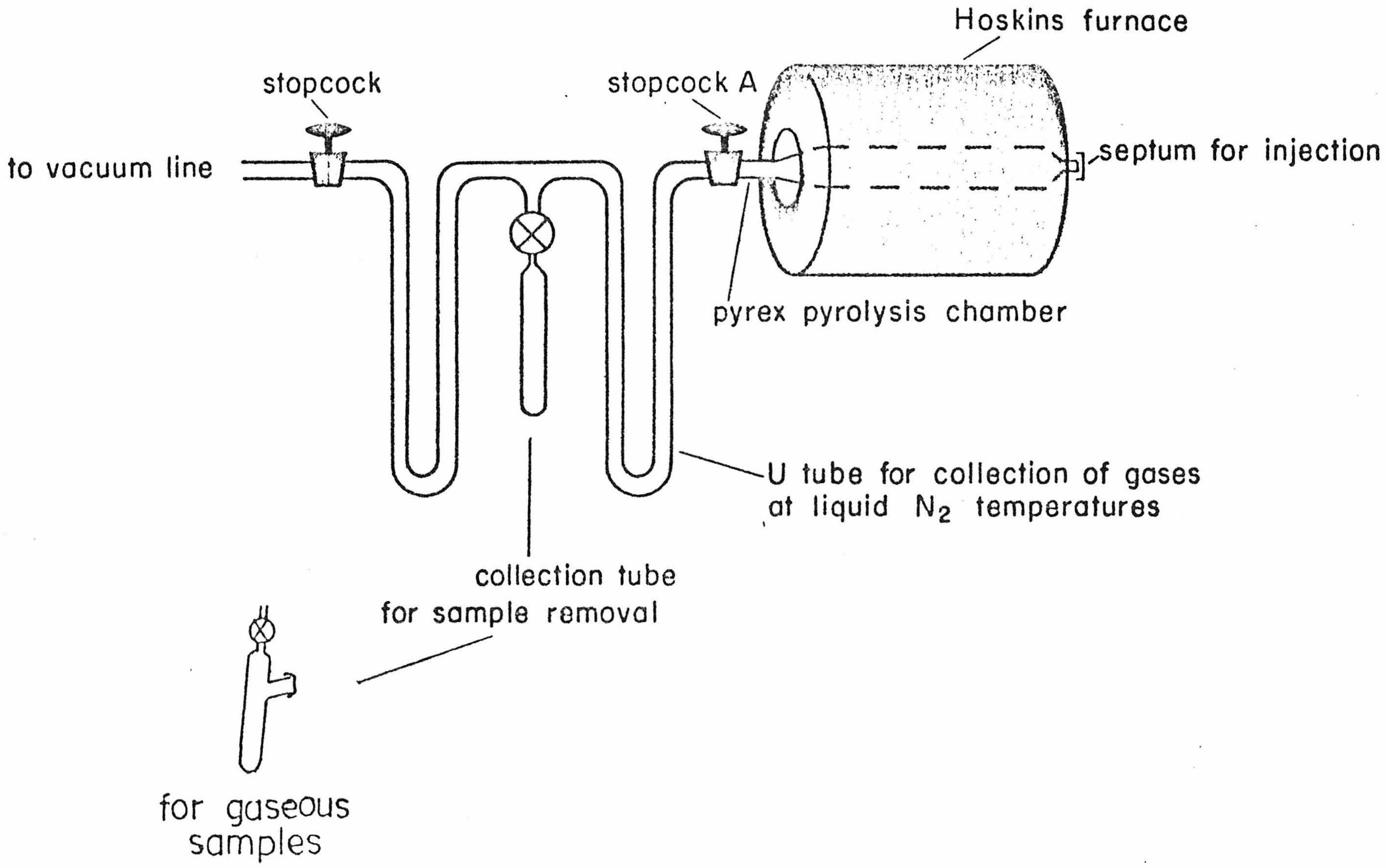
The oxidation of *trans*-3,4-hydrazo compound **18** to *trans*-3,4-azo compound **3** was complete in 24 hr affording a 1:1 mixture of *trans*-3,4-dimethyl-3,4,5,6-tetrahydropyridazine (**3**) and the corresponding hydrazone, *trans*-3,4-dimethyl-3,4,5,6-tetrahydropyridazine (**29**).

Azo **3**: NMR (C_6D_6): δ 0.45-2.6 (m, 11), 0.61 (d, J = 6.0Hz), 0.73 (d, J = 6.3Hz), 6.61 (m, 1). Hydrazone **29** was purified by preparative VPC (Pennwalt, 180°). NMR (C_6D_6): δ 0.45-2.6 (m, 11), 0.60 (d, J = 6.0Hz), 0.73 (d, J = 6.3Hz), 6.6 (m, 1).

Thermal Reactions

The pyrolyses were carried out in a 2.8 x 30 cm cylindrical Pyrex tube, with a 0.6 x 3 cm injector port with serum cap, mounted in a Hoskins type FD 303A tube furnace. The other end of the tube was connected via a 6 mm bore stop-cock (A) to a high vacuum line equipped with two liquid nitrogen cooled u-shaped taps plus a small receiving tube. The temperature was measured by a thermometer inserted into the furnace or an iron-constantan thermocouple connected to a potentiometer. Before pyrolysis the tube was evacuated and stop-cock A was closed. In a typical run, 10 μℓ of the solution (~ 10% azo in C_6D_6) was injected through the serum cap via a gas tight syringe. After pyrolyses times of 5 to 30 sec, stop-cock A was opened and the pyrosylate was collected in the liquid nitrogen cooled traps. The hydrocarbon contents of the traps were transferred to the receiving tube which was sealed with a torch and removed for analysis (see diagram).

The pyrosylate tube was cooled to 77°K, opened and the contents diluted with 20 μℓ of toluene. The products were analyzed immediately by analytical VPC (DBT and ODPN, 25°). Assignment of the product peaks was carried by coinjection techniques using authentic samples. Relative retention times are as follows: (DBT, 25°): ethylene (0.101), <u>trans-</u>


Hoskins furnace
stopcock
stopcock A
to vacuum line
septum for injection
pyrex pyrolysis chamber
U tube for collection of gases
at liquid N_2 temperatures
collection tube
for sample removal
for gaseous
samples

2-butene (0.211), cis-2-butene (0.233), trans-1,2-dimethylcyclobutane (0.650), cis-1,2-dimethylcyclobutane (1.00). (ODPM, 25°): ethylene (0.55), cis- and trans-2-butenes (0.69, trans-1,2-dimethylcyclobutane (0.82), 3-methyl-1-pentene (0.90), cis-1,2-dimethylcyclobutanes (1.00). Each of the four azo isomers were synthesized four different times. Each sample was pyrolyzed at least three times. Analytical VPC analysis was carried out at least twice on each run. The DBT column was used to analyze the olefin and cyclobutane ratios except that the 3-methyl-1-pentene and trans-1,2-dimethylcyclobutane peaks overlapped. The ODPM column separated these two products and made possible the calculation of the relative yields of all of the hydrocarbon products.

Controls

a) The hydrazones 28 and 29 were shown not to give any of the azo decomposition hydrocarbon products under identical pyrolysis conditions.

b) The products 1,2-dimethylcyclobutanes and 2-butenes were shown to be stable to isomerization under the pyrolysis conditions.

c) The ratio of labile azo compound to internal standard ethyl ether in benzene-d_6 was determined by NMR. After pyrolysis the ratio of hydrocarbon products/ethyl ether afforded a rough estimate of mass balance. The remaining labile azo compound rearranged irreversibly to the corresponding hydrazone. Pressure effects (135-320 Torr) were checked by adding n-octane or n-pentane to the pyrolysis tube before the azo compound in benzene-d_6. None were found. Surface effects were checked by repeating all the pyrolyses with the tube filled with glass chips. None were found.

EXPERIMENTAL SECTION (Part II)

Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by the Caltech Analytical Facility and Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Infrared spectra (IR) were recorded on a Perkin-Elmer Model 257 Infrared spectrophotometer except for gaseous samples which were recorded on a Beckman IR 42-10 instrument. For quantitative analyses, IR spectra were recorded on a Perkin-Elmer Model 180, infrared spectrophotometer.[12] Nuclear magnetic resonance (NMR) data were recorded on a Varian EM390 NMR spectrometer. Chemical shifts are given as parts per million (ppm) downfield from Me_4Si in δ units and coupling constants in cycles per second (Hz). NMR data are reported in this order: chemical shift; multiplicity, s = singlet, d = doublet, t = triplet, m = multiplet, number of protons; coupling constants, assignment. Electronic spectra were recorded on a Beckman Model 25 spectrophotometer. Mass spectra were recorded on a DuPont 21-492B mass spectrometer except for ethylene and cyclobutane samples which were recorded on an ion cyclotron resonance spectrometer (ICR) built at Caltech.[20]

For analytical vapor-phase chromatography (VPC), a Hewlett-Packard 5700 A Gas Chromatograph equipped with a flame ionization detector and nitrogen carrier gas was used. The 0.125 in. packed stainless steel columns used in this instrument are listed in Table 10. Quantitative VPC analysis was accomplished using a Hewlett-Packard 3370A electronic digital integrator. For preparative VPC, a Varian Aerograph Model 920 instrument, equipped with a thermal conductivity detector and helium carrier gas was used. The 0.375 in. packed aluminum columns used are listed in Table 10. Gas samples were separated and collected on a Varian Aerograph Model 90-P instrument equippped with a gas inlet and collection system.

Diglyme and tetrahydrofuran were distilled from sodium metal. Pyridine was distilled from sodium hydroxide and stored over barium oxide.

Dimethyl-3,4,5,6-Tetrahydropyridazine-1,2-dicarboxylate, (23-d_0).

A solution of 6g (30 mmol) of dimethyl-3,6-dihydropyridazine-1,2-dicarboxylate, obtained from the Diels-Alder reaction of 1,3-butadiene and dimethyl azodicarboxylate, in 50 ml of ethanol was hydrogenated over 0.1g of platinum oxide. The solution was filtered, concentrated, and distilled yielding 5.5g (90%) of the saturated diurethane

Table 10

VPC Columns

Designation	Description
SE-30	20' x 0.375", 25% SE-30 on 100/120 Chromosorb P
Carbowax 20M	10' x 0.375", 25% Carbowax 20M on 60/80 Chromosorb W
ββ'	10' x 0.375", 25%, β,β'-oxydipropionitrile on 60/80 Chromosorb P
FFAP	10' x 0.375", 25% FFAP on 60/80 Chromosorb W
SF-96	5' x 0.375", 10% SF-96 on 60/80 Chromosorb W
Pennwalt	6' x 0.25", glass, Pennwalt 223 amine packing (Applied Sciences Laboratories, Inc.)
SE-30	10' x 0.125", 30% SE-30 on 100/120 Chromosorb P
Poropak N	6' x 0.125", Poropak N, 100/120 mesh
DBT	20' x 0.125", 10% dibutyltetrachlorophthalate on 100/120 Chromosorb P
ODPN	15' x 0.125", 10% β,β'-oxydipropionitrile on 100/120 Chromosorb P

(23-d_0): bp 90-95° (0.3 mm), mp 40.5-41.5°; IR (CCl_4) 1710 (C=O); NMR ($CDCl_3$) δ 1.5-1.9 (m, 4), 2.7-3.2 (m, 2), 3.75 (s, 6), 4.0-4.4 (m, 2); mass spectrum: m/e 202.

Anal. Calcd. for $C_8H_{14}N_2O_4$: C, 47.52; H, 6.98; N, 13.85. Found: C, 47.31; H, 6.92; N, 13.52.

cis-3-Buten-1-yl-3,4-d_2 Acetate (20).

Borane-d_3 (0.27 mol) was generated in a flame-dried flask under a nitrogen atmosphere from the dropwise addition of 75 ml (0.61 mol) of boron trifluoride etherate to a stirred slurry of 12.6g (0.30 mol) of lithium aluminum deuteride (98% d) in ether at 0° and distilled through a cooled condenser (-78°) into 300 ml of dry tetrahydrofuran. To the 0.90 M solution of borane-d_3 in tetrahydrofuran was added 55 ml (0.54 mol) of cyclohexene at 0°. A white precipitate formed and the reaction mixture was allowed to stir for 1 hr at 0°. 3-Butynyl acetate (22g, 0.19 mol), obtained from the reaction of 3-butyn-1-ol with acetyl chloride in pyridine, was added to the dicyclohexyl borane-d_1. The reaction mixture was allowed to stir at 0° for 2 hr. The solution became clear and 95 ml of acetic acid-O-d (98% d) was added. This was allowed to stir at 25° for 1 hr. A solution of 50g of sodium hydroxide in 150 ml of water was added slowly followed by 100 ml of 30% hydrogen peroxide. After 1 hr the tetrahydrofuran layer was separated. The aqueous layer was extracted once with ether. The organic layers were combined, dried (Na_2SO_4), and distilled. One fraction (bp 70-130°) was collected. Analytical vapor phase chromatography (Carbowax 20M, 120°) indicated this fraction contained tetrahydrofuran, 3-butenyl acetate (20), cyclohexyl acetate, and cyclohexanol and no 3-butynylacetate, by comparison with authentic samples. This 3-butenyl acetate (20) was purified by preparative vapor phase chromatography (Carbowax 20M, 120°) for analysis: IR (CCl_4) 2950 (C-H), 2250 (C-D), 1745 (C=O); NMR ($CDCl_3$) δ 2.0 (s, 3), 2.3 (broad t, 2, J = 6Hz), 4.1 (t, J = 6Hz), 5.0-5.1 (m, 1.06 ± 0.02); mass spectrum: m/e 116, 115.

cis-3,4-Epoxybutan-1-yl-3,4-d_2 Acetate (21).

To a stirred solution of 10 ml of dichloromethane and 1g (8.6 mmol) of *cis*-3-buten-1-yl-3,4-d_2 acetate was added 3g (19.6 mmol) of *m*-chloroperbenzoic acid in 50 ml of dichloromethane. After stirring for 4 hr at room temperature, the solution was washed with saturated aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride. The solution was dried (Na_2SO_4), filtered, and concentrated.

The remaining liquid was distilled: bp 48-49° (0.5 mm) and further purified by vapor phase chromatography (SF-96, 75°) affording 1g (7.5 mmol) of the epoxide-d_2 21 (87%) IR (CCl_4) 2940 (C-H), 2210 (C-D), 1740 (C=O), 1350, 1220, 1030; NMR ($CDCl_3$) δ 1.7-2.0 (m, 2), 2.0 (s, 3), 2.45 (s, 1), 2.75 (m, 0.09 ± 0.02), 4.2 (t, 2, J = 6Hz).

3,4-Epoxybutan-1-yl Acetate (21-d_0).

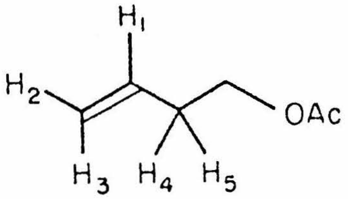
For comparison, the non-deuterated epoxide was prepared in the same manner from 3-butene-1-yl acetate: bp 48-49° (0.5 mm); IR (CCl_3) 3030, 2980 (C-H), 1740, 1220, 1050, 900, 830; NMR ($CDCl_3$) δ 1.7-2.0 (m, 2), 2.0 (s, 1), 2.40-2.53 (m, 1), 2.67-2.80 (m, 1), 2.82-3.07 (m, 1), 4.2 (t, 2, J = 6Hz).

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.37; H, 7.75. Found: C, 55.16; H, 7.59.

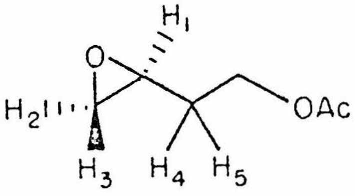
The isomeric and isotopic purity of cis-3-buten-1-yl-3,4-d_2 acetate was determined by conversion to the epoxide which allows the terminal hydrogens could be distinguished.[22] The 4 position of the acetate contained 1.06 ± 0.02 hydrogens by NMR integration (standard deviation of four integrations). The chemical shifts of H_1, H_2, and H_3 of epoxide 21-d_0 are δ 2.9, 2.7, and 2.5 respectively. Position 2 contains 0.09 ± 0.02 hydrogens and position 1 contains < 0.02 hydrogens for epoxide 21 (standard deviation of 10 integrations). See Table 11. Therefore, since the starting olefin contains 6% excess hydrogen in the terminal positions, 3 ± 3% hydrogen (9(±2) - (6(±2)) is in the 2 position instead of deuterium. Therefore one may conclude that for the d_2 compound, all of the deuterium is in the 1 and 2 positions within the limits of NMR integration.

Table 11

NMR Integrations of 20 and 21 for the Determination of the Stereochemical and Isomeric Purity of 20.



20



21

Compound	Integrations			
	H_1	$H_2 + H_3$	$H_4 + H_5$	
20-d_0	1.00	2.00	2.00	
20	--	1.06 ± 0.02	2.00	
	H_1	H_2	H_3	$H_4 + H_5$
21-d_0	1.00	1.00	1.00	2.00
21	< 0.02	0.09 ± 0.02	1.00	2.00

Dimethyl *cis*-3,4,5,6-Tetrahydropyridazine-1,2-dicarboxylate-3,4-d_2 (23).

The synthesis of butane-1,4-diol-1,2-d_2 by the hydroboration of 20 was accomplished using the method of Brown and Unni.[23] The aqueous layer was extracted with ether for four days by liquid-liquid extraction. Careful addition of sodium bisulfite to the ether extract quenched the excess hydrogen peroxide. The ether solution was dried (Na_2SO_4) and concentrated affording a mixture of 1,4- and 1,3-diols (4.8/1 ratio, respectively). This was dissolved in 160 ml of dry prydine and cooled to -42°. Methanesulfonyl chloride was added dropwise over 40 min to the cooled reaction mixture with stirring. The reaction mixture was allowed to warm to 25°, and then stirred for 1 hr. This was poured over 250 ml of crushed ice and left to stand 12 hrs. A white precipitate formed. This was collected by filtration, dissolved in methylene chloride, washed with aqueous sodium chloride, dried (Na_2SO_4), and concentrated affording 9.8g of a white powder. From the ratio of diols, 8.1g (33 mmol) is the desired *threo*-1,4-butanediyl-1,2-d_2 dimethanesulfonate 22 (17% yield from 3-butynyl acetate): NMR ($CDCl_3$) δ 1.7-1.9 (m, 3), 3.0 (s, 6), 4.1-4.3 (m, 3). The crude dimesylate 22 was used without further purification.

To a solution of 6.0g (34 mmol) of dimethyl hydrazine dicarboxylate in 50 ml of diglyme was added 1.9g of sodium hydride (50% mineral oil dispersion, 34 mmol) under a nitrogen atmosphere. After vigorous stirring for 3 hr at 25°, a solution of 9.8g of the crude mesylate (containing 33 mmol of threo-1,4-butane-diyl-1,2-d_2 dimethanesulfonate 22) in 30 ml of dry diglyme was added. The reaction mixture was allowed to stir under reflux for 24 hrs, then allowed to cool. Dry diglyme (50 ml) and 1.9g of sodium hydride were added.[11] This was allowed to reflux for 24 hr and then cooled to room temperature. The reaction mixture was filtered. The filtrate was diluted with 25 ml of water and extracted with 200 ml of ether. The etheral extract was dried (Na_2SO_4) and concentrated under reduced pressure. The concentrate was extracted with 30 ml of hexane. This was concentrated and distilled: bp 85-95° (3 mm). The distillate was further purified by preparative vapor phase chromatography (FFAP, 190°) affording 2g (10 mmol) of the saturated diurethane 23 (30%): mp 40.5-41.5°; IR (CCl_4) 2940 (C-H), 2150 (C-D), 1710 (C=O); NMR ($CDCl_3$) δ 1.6-1.8 (m, 3), 2.8-3.0 (m, 1.5), 3.7 (s, 6), 4.0-4.2 (m, 1.5); mass spectrum: m/e 204, 203 (d_2/d_1 = 93/7).

Anal. Calcd. for $C_8H_{12.07}N_2O_4D_{1.93}$: C, 47.07;, H, 6.91; N, 13.12. Found: C, 47.44; H, 6.97; N, 13.41.

Hexahydropyridazine and *cis*-Hexahydropyridazine-3,4-d_2 (24).

The undeuterated and *cis*-3,4-d_2 diurethane 23 were hydrolyzed in the same manner. The diurethane 23 (0.5g, 2.5 mmol) was added to 1g (18 mmol) of potassium hydroxide dissolved in 10 ml of thoroughly degassed water. The reaction mixture was allowed to reflux with stirring for 24 hr under a nitrogen atmosphere. The solution was cooled to 0°, 4 ml of degassed 6N HCl was added via syringe, and the reaction mixture was allowed to stir for 0.5 hr at 25°. Then, 12 ml of degassed aqueous saturated potassium carbonate was added, and the reaction mixture was extracted three times with 25 ml portions of ether, which was freshly distilled from calcium hydride under a nitrogen atmosphere and delivered via a double-ended needle. Each extract was transferred by a stream of nitrogen via a double-ended needle to a pressure equalized funnel, containing $MgSO_4$ in a filter thimble attached to the top of a distillation head. After the ether solvent was removed by distillation through a 6 in. vigreux column, the remaining oil was distilled on a vacuum line (10^{-4} Torr). The clear, colorless hydrazo distillate was transferred into an NMR tube on the vacuum line and diluted with *ca*. 0.5 ml of degassed benzene-d_6. The NMR tube was sealed and removed.

Hexahydropyridazine (24-d_0).

NMR (C_6D_6): δ 1.3 (quintet, 4, J = 3Hz), 2.1 (broad s, 2), 2.6 (broad quintet, 4, J = 3Hz).

cis-Hexahydropyridazine-3,4-d_2 (24).

NMR (C_6D_6): δ 1.3 (broad t, 3, J = 3Hz), 2.3 (broad s), 2.6 (m, 6).

Preparation of 3,4,5,6-Tetrahydropyridazine and *cis*-3,4,5,6-Tetrahydropyridazine-3,4-d_2 (6).

Both hydrazines (24) were oxidized in the same manner. A solution of the hexahydropyridazine (24) in benzene-d_6 was allowed to stand in the dark under a positive pressure of oxygen for 6 hr. The reaction was monitored by NMR.

After 6 hr, the solution consisted of 50% azo, 30% hydrazo and 20% of the corresponding hydrazone.

3,4,5,6-Tetrahydropyridazine (6-d_0).

UV max (C_6D_6) 375 nm; NMR (C_6D_6) δ 0.8-1.0 (m, 4H), 3.4-3.6 (m, 4H).

The corresponding hydrazone was obtained by allowing the azo compound (6) to stand four days at room temperature. The hydrazone was isolated by preparative VPC (Pennwalt 223, 170°). NMR (C_6D_6) δ 1.5-1.8 (m, 4), 2.5-2.8 (m, 2), 4.3-5.3 (broad s, 1), 7.5-7.7 (m, 1).

cis-3,4,5,6-Tetrahydropyridazine-3,4-d_2 (6).

NMR (C_6D_6) δ 0.8-1.0 (m, 3H), 3.4-3.6 (m, 3H).

cis-Ethylene-1,2-d_2 (25)[13]

Acetylene-d_2 was synthesized by the reaction of calcium carbide (Fisher 20-30 mesh) and deuterium oxide. Reduction of this acetylene-d_2 (27) with zinc-copper couple, from the reaction of zinc dust and an aqueous solution of cupric sulfate, in the presence of HCl afforded cis-ethylene-1,2-d_2 (25). The ethylene-1,2-d_2 (25) was further purified by preparative VPC (SE-30, 25°): IR (gas) 842, (987 and 724 $< 1\%$); ms (12 ev) m/e 30, 29, 28, (ratios 72.6, 21.0, 6.4 ± 1%). The mass spectrum was run under conditions where ethylene gave only one peak at m/e: 28. Analysis by an analytical VPC (Poropak N, 70°) revealed 2.1% acetylene present which accounts for 33% of the m/e = 28 peak.

trans-Ethylene-1,2-d_2 (26)[13]

Reduction of acetylene-d_2 (27) by aqueous chromous chloride afforded trans-ethylene-1,2-d_2 (26). This was purified by preparative VPC (SE-30, 25°). IR (gas) 987, 742, (842 $< 1\%$); mass spectrum: (ev) m/e: 30, 29, 28 (ratios: 56.4:30.9:12.7 ± 1%). Analysis by analytical VPC (Poropak N, 70°) revealed 0.3% acetylene present.

cis-1-Cyclobutanol-2-d_1 (30).

Cyclobutene[24] (34) (1 ml, 13.6 mmol) was bubbled by a stream of nitrogen via a double-ended needle into a flask containing 20 ml of dry tetrahydrofuran at 0° equipped with a condenser (-78°). Borane-d_3, generated as described previously using 0.25 (5.9 mmol) of lithium aluminum deutride (98%-d) and 1.5 ml (12.0 mmol) of borontrifluoride etherate, was bubbled into the cyclobutene/tetrahydrofuran solution. This was allowed to stir at 0° for 1 hr. Water (2 ml) was added to quench excess hydride and the solution was heated to 40°. Then 3 ml of 3N sodium hydroxide was added, followed by 3 ml of 30% hydrogen peroxide. The solution was allowed to stir for 1 hr at 40°, extracted three times with 30 ml portions of ether, washed with saturated aqueous sodium chloride, dried (Na_2SO_4), and concentrated. The cyclobutanol product (30) (0.6g, 8.2 mmol) (60%) was isolated by preparative VPC. (Carbowax 20M, 140°): IR (CCl_4) 3600 and 3300 (O-H), 2970 (C-H), 2190 and 2200 (C-D), 1460. NMR ($CDCl_3$) δ 1.2-2.5 (m, 5), 3.3 (broad s, 1), 4.0-4.4 (m, 1).

cis-1-Cyclobutanyl-2-d_1 Tosylate (31).

cis-1-Cyclobutaneol-2-d_1 (30) (0.3g, 4.1 mmol) was dissolved in 15 ml of dry pyridine. This was cooled to 0° and 3.8g (20 mmol) of tosyl chloride was added under an inert atmosphere. The reaction mixture was kept at 5° for 12 hr, diluted with 14 ml of ice cold water, extracted with 25 ml portions of ether, washed three times with 20 ml portions of ice cold 1M HCl and once with ice cold water and saturated aqueous sodium chloride. The ether layers were combined, dried (Na_2SO_4) and concentrated affording 0.4g (1.65 mmol) of tosylate 31 (40%): NMR ($CDCl_3$) δ 1.4-2.4 (m, 5), 2.45 (s, 3), 4.5-5.0 (m, 1), 7.2-7.9 (m, 4).

trans-Cyclobutane-d_2 (8).

To 15 ml of a 1M solution of lithium triethylborodeuteride in dry tetrahydrofuran (Superdeuteride from Aldrich, 98% d_1) at 0° was added 0.4g (1.6 mmol) of cis-1-cyclobutanyl-2-d_1 tosylate (31) in 7 ml of dry tetrahydrofuran. The reaction mixture was stirred at 0° for 15 min, then at 25° for 90 min under a flow of nitrogen gas. The nitrogen carrier gas was passed through a drying tower ($CaCl_2$) into a u-tube cooled to -78°. The reaction mixture was heated to 50° for 1 hr to drive the gaseous products into the u-tube. The products collected were cyclobutane and tetrahydrofuran. No other C_4 gases were formed in the reaction. The trans-cyclobutane-1,2-d_2 was isolated by preparative VPC (SE-30, 25°), IR (gas) 2950 (C-H), 2190 (C-D), 1450 (CH_2), 1294, (CHD), 579, 543, (562 < 2%);

mass spectrum (9.0 ev) m/e: 58, 57, 56 (d_2/d_1 = 95.5/4.5 ± 1 by comparison with cyclobutane under the same conditions).

trans-1-Cyclobutanol-2-d_1 (32).

Cyclobutane oxide (33), synthesized from cyclobutene as described by Ripoll and Conia,[25] was purified by preparative VPC (ββ, 85°). To 15 ml of a 1M solution of lithium triethylborodeuteride in dry tetrahydrofuran (Superdeuteride, 98% d_1) at 0° was added 0.5g (7.1 mmol) of cyclobutene oxide in 5 ml of dry tetrahydrofuran. Excess hydride was quenched with water after 1 hr. Hydrogen peroxide solution (30%, 3 ml) was added until no reaction occurred. Then 10 ml of ether was added followed by potassium carbonate until the two layers separated. The aqueous layer was extracted with two 10 ml portions of ether, and the ether layers were combined with the ether/tetrahydrofuran layer, dried (Na_2SO_4) and concentrated. The cyclobutanol product (32) was purified by preparative VPC (Carbowax, 140°) affording 0.5g (6.95 mmol) of trans-1-cyclobutanol-2-d_1 (32) (96%). IR (CCl_4) 3600 (O-H), 2980 (C-H), 2200 (C-D), 1460; NMR ($CDCl_3$) δ 1.1-2.4 (m, 6), 3.0 (broad s), 3.9-4.4 (m, 1).

cis-Cyclobutane-1,2-d_2 (7), Method A

Successive treatment of trans-1-cyclobutanol-2-d_1 (32) with tosyl chloride and lithium triethylborodeuteride (as reported above for cis-1-cyclobutanol-2-d_1 (30)) afforded cis-cyclobutane-1,2-d_2 (7) which was isolated by preparative VPC (SE-30, 25°). IR (gas) 2990 (C-H), 2200 (C-D), 1450 (CH_2), 1307 (CHD), 569, 562 (1294 $<$ 2%); mass spectrum (90 ev) m/e: 58, 57, 56 ($d_2/d_1 = 95.5/4.5 \pm 1$ by comparison with cyclobutane under the same conditions).

cis-Cyclobutane-1,2-d_2 (7), Method B

Cyclobutene (34) (1 ml, 13.6 mmol) was added via a condenser (-78°) to 40 ml of ethanol-0-d_1 (Aldridch, 99.5% d_1) and 9.0g (56 mmol) of potassium azodicarboxylate.[26] Acetic acid-0-d (Aldrich, 98% d) was added dropwise via a dropping funnel and the reaction mixture was maintained at 0° for 90 min. The reaction mixture was heated slowly to 50° over 90 min and then cooled. The -78° condenser was replaced with a 25° condenser and the ethanol was refluxed for 1 hr under a stream of nitrogen gas which was passed through a u-tube cooled to -78° in order to collect the volatile products. Analytical VPC (SE-30, 25°) indicated the products (∿ 2 ml) to consist of a 90/10 mixture of cyclobutane and cyclobutene, relative retention times 1.0 and 0.81, respectively. The cis-cyclobutane-1,2-d_2 (7)

was isolated by preparative VPC (SE-30, 25°). The spectral properties were identical with the cis-cyclobutane-1,2-d_2 (7) obtained by Method A. Mass spectral analysis revealed a d_2/d_1 ratio of 89.3/10.7 ± 1.

Cyclobutane-d_1 (35).

Similar to procedures described above, reaction of cyclobutanyl tosylate (36-d_0) with lithium triethylborodeuteride (Superdeuteride, 98% d_1) afforded cyclobutane-d_1 (35). IR (gas) 2990, 2200, 1450, 1307.

Thermal Reactions

The pyrolyses were carried out in a 2.8 x 30 cm cylindrical Pyrex tube, with a 0.6 x 3 cm injector port with a serum cap, mounted in a Hoskins type FD 303 A tube furnace. The other end of the tube was connected via a 6 mm bore stopcock (A) to a high vacuum line equipped with two liquid nitrogen cooled u-shaped traps plus a small receiving tube equipped with a stopcock and a sidearm sealed with a serum cap. The temperature was measured by an Omega digital thermometer with an iron-constantan thermocouple. Before pyrolysis, the tube was evacuated and stopcock A was closed. In a typical run for VPC analysis, 10 ul of the solution (10% azo in C_6D_6) was injected through the serum cap via a gas tight syringe. For infrared analysis, 150 ul injections were made (the product ratios were unchanged). After pyrolyses times of 5 or 30 sec, stopcock A was opened and the pyrosylate was collected in the liquid nitrogen-cooled traps. The hydrocarbon contents of the traps were then transferred into the receiving tube; its stopcock was closed, and the tube was removed from the vacuum line for analysis.

Upon warming to room temperature, the entire sample vaporized in the tube. A gas syringe (precision Sampling Model "Pressure-Lok" Series A) was inserted through the serum cap and 2.5 ml of the gas sample was collected. The sample was sealed in the syringe and the needle was removed from the collection tube. The products could then be analyzed by VPC (SE-30, 25°). Assignments of the product peaks were made by coinjection techniques using authentic samples. The response factors for ethylene and cyclobutane was found to be 1.07 ± 0.02 to 1.00, respectively by calibration with authentic mixtures.

Relative retention times are as follows (SE-30, 25°): ethylene (0.181), propylene (0.295), 1-butene (0.595), cyclobutane (1.00). Each of the azo compounds was synthesized at least twice and each sample was pyrolyzed at least twice. The results are given in Table 4.

For samples which were analyzed by infrared spectroscopy, three 150 ul injections were pyrolyzed and collected in a collection tube equipped with a stopcock. Ethylene and cyclobutane were separated by gas chromatography (SE-30, 25°) on a Varian Aerograph Model 90-P instrument equipped with a gas inlet and collection system. The samples were stored in vacuum bulbs equipped with stopcocks. The IR analyses are described below.

Infrared Analysis of Pyrolysis Products

The ethylene and cyclobutane samples, purified by VPC as described above, were analyzed by infrared spectroscopy with a Perkin-Elmer Model 180 infrared spectrometer in the absorbance mode.[12] The wavelengths were not calibrated. The cell used for gas sampling had a path length of 8 cm and a volume of 8 ml. The cell was equipped with a cold finger so samples could be vacuum transferred into it.

Ethylene was analyzed using the 842 cm^{-1} band for cis-ethylene-1,2-d_2 and the 724 cm^{-1} band for trans-ethylene-1,2-d_2.[13] Ethylene-d_1 has a band at 809 cm^{-1}, and ethylene (half of the ethylene products from the pyrolyses of 6 is nondeuterated) has a band at 945 cm^{-1}.

These peaks did not interfere with the analyses, although use of the 987 cm^{-1} band from trans-ethylene-1,2-d_2 was precluded. A sample for IR analysis was prepared by pyrolyzing the azo compound 6 synthesized from 0.5-0.75g of the diurethane by three 150 ul injections. Three samples were analyzed.

Two methods were used to obtain the relative ratio of cis/trans-ethylene-d_2 (25/26). First, since the relative amount of d_2 to d_1 compound in the authentic samples was known by mass spectrometry, the relative extinction coefficients between cis-ethylene-1,2-d_2 and ethylene-d_1 and between trans-ethylene-1,2-d_2 and ethylene-d_1 could be determined. Therfore, the relative extinction coefficient between cis- and trans-ethylene-d_2 could be calculated. See Table 6 for the results. Second, known mixtures of authentic samples were made up using an MKS Vacuum transmitter type 221 pressure gauge. The pressure (± 0.005 Torr) of a fixed volume of sample was measured and transferred into a bulb followed by a measured amount of another sample. The mixture was vacuum transferred into the gas cell for infrared analysis. This sample was collected again, measured, and more of one isomer was added, etc. See Table 6 for the results. (The pressure of ethylenes in the IR gas cell was ca. 50 Torr for the authentic mixtures and for the pyrolyses products.)

Two modes of operation of the spectrometer were used. In one mode, "manual slit", the slit width is kept constant while the gain is varied to keep the reference beam energy constant during the scan. In the other mode, "constant Io" the slit width is varied while the gain is kept constant. These results are record in Tables 6 and 12.

Table 12

Analysis of Ethylene-d_2 Products from the Pyrolysis 6

cis/trans-ethylene-1,2-d_2	IR Peak Height Ratio[a] (842 cm^{-1}/724 cm^{-1})
5.25[b]	4.1
4.0[b]	3.2
1:1[c]	0.93
pyrolysis of 6[d]	3.85 ± 0.10

[a] Infrared Mode of Operation: Constant Io mode.

[b] Authentic mixture ratios (see footnote b, Table 6).

[c] Relative extinction coefficient (see footnote e, Table 6).

[d] Chamber pyrolysis (5s at 439 ± 5°, est. pressure 300 mm).

The value obtained for cis/trans-ethylene-1,2-d_2 ratio using the relative extinction coefficient of the 842 and 724 cm^{-1} bands in the constant Io mode is 80.5/19.5 which compares favorably with the values obtained using the constant slit mode (80.6/19.4). The interpolated value, however, is significantly different (82.8/17.2) and is dropped since the difference could be due to an error in one of the two authentic mixtures. (This problem cannot occur using the relative extinction coefficients.)

The cis and trans ratios of the cyclobutane products (7 and 8) of the pyrolysis were analyzed by measuring the relative ratios of the 1307 (cis-7) and 1294 cm^{-1} (trans-8) bands. One sample was analyzed. This sample was obtained from the total pyrolysis of the azo compound synthesized from two 0.75g samples of the diurethane. The total pyrolysis required six ca. 150 ul pyrolyses. Mass spectral analysis showed the cyclobutane from pyrolysis to be 92.5% d_2 and 7.5% d_1 ± 1%. Since cyclobutane-d_1 has a band at 1307, calibration mixtures of authentic samples must have cyclobutane-d_1 present. Since the authentic trans-cyclobutane-1,2-d_2 contains 4.5% cyclobutane-d_1 and the cis-cyclobutane-1,2-d_2 contained 10.7% cyclobutane-d_1, a 50:50 mixture would contain 7.6% of the cyclobutane-d_1. This alleviated the necessity of adding more cyclobutane-d_1 to the authentic mixtures.

The mixtures were prepared in the same manner as described for ethylene. The results are given in Table 5. The spectrum of each mixture was taken three times while the spectrum of the pyrolysis product was taken four times. (The pressure in the IR gas cell was ca. 20 Torr for the cyclobutane analyses.)

The spectra were enlarged five times for analysis. Without enlargement, the 1307:1294 ratio was 1.54 ± 0.13 for the pyrolysis product.

Due to the low yield of cyclobutane and the small extinction coefficients of the infrared bands used for analysis, the product of six pyrolyses were combined. Other ratios which could be measured individually for each pyrolyzed sample of 32 (ethylene/cyclobutane and *cis*/*trans*-ethylene-1,2-d_2) were unchanged from sample to sample.

IR Spectra

Sample infrared spectra are shown in Figures 2-11. Figures 2 and 3 are the spectra of isomerically pure samples of *cis*- and *trans*-ethylene-1,2-d_2 respectively. (The small peak at ≈ 730 cm^{-1} in the *cis*-ethylene sample is due to the 2% acetylene-d_2 impurity present. This peak had to be taken into account in the authentic mixtures since it has a shoulder at 724 cm^{-1}, where the *trans*-ethylene-1,2-d_2 peak occurs.) Figures 4-6 are authentic mixtures of *cis*- and *trans*-ethylene-1,2-d_2. The ratios of *cis* to *trans*-ethylene-1,2-d_2 in these spectra are 84/16, 79/21 and 74/26 respectively. Figure 7 is an infrared spectrum of the ethylene products from the pyrolysis of 6.

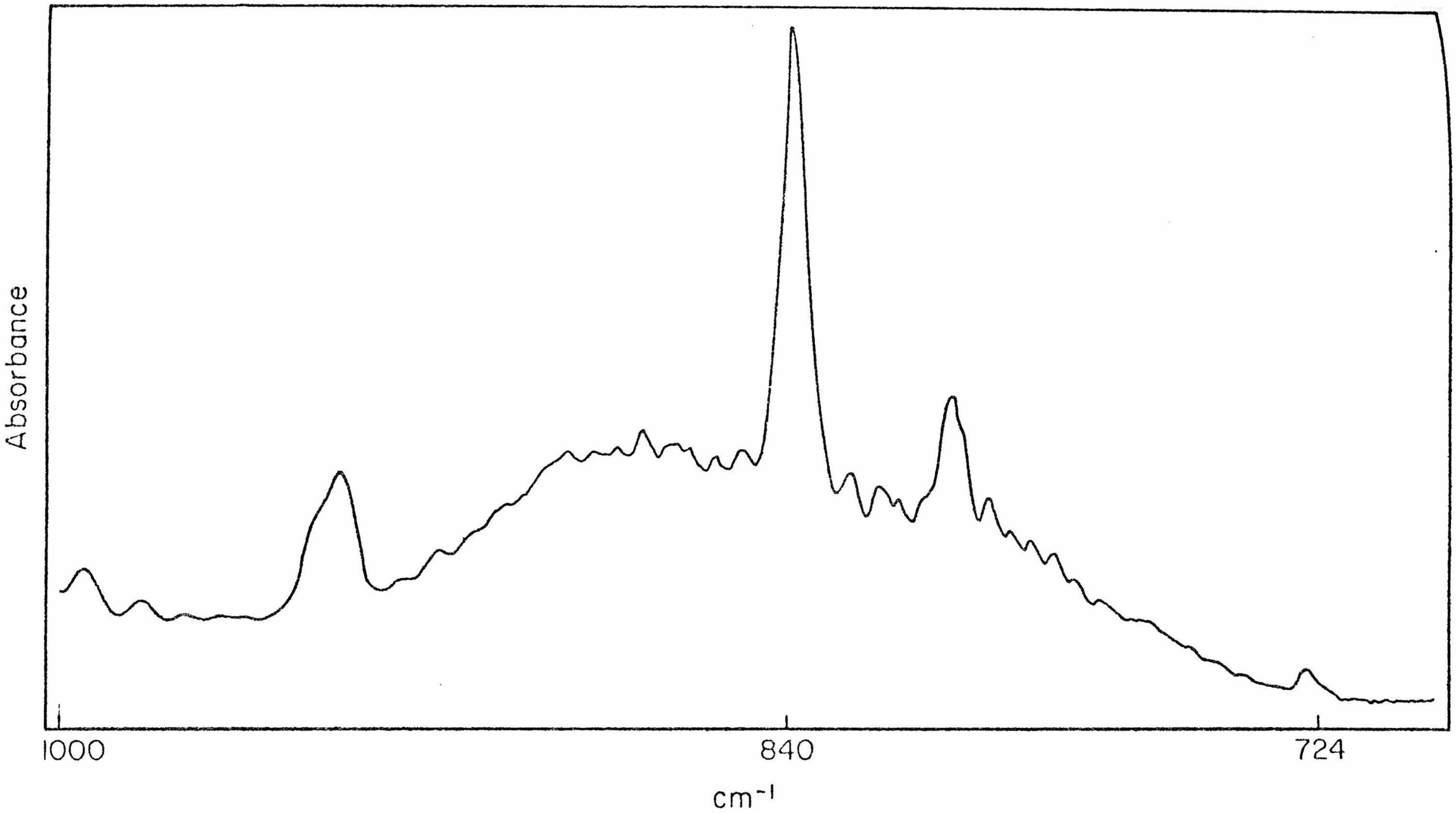


Figure 2. Infrared spectrum of cis-ethylene-1,2-d_2 (includes ethylene-d_1 and d_0)

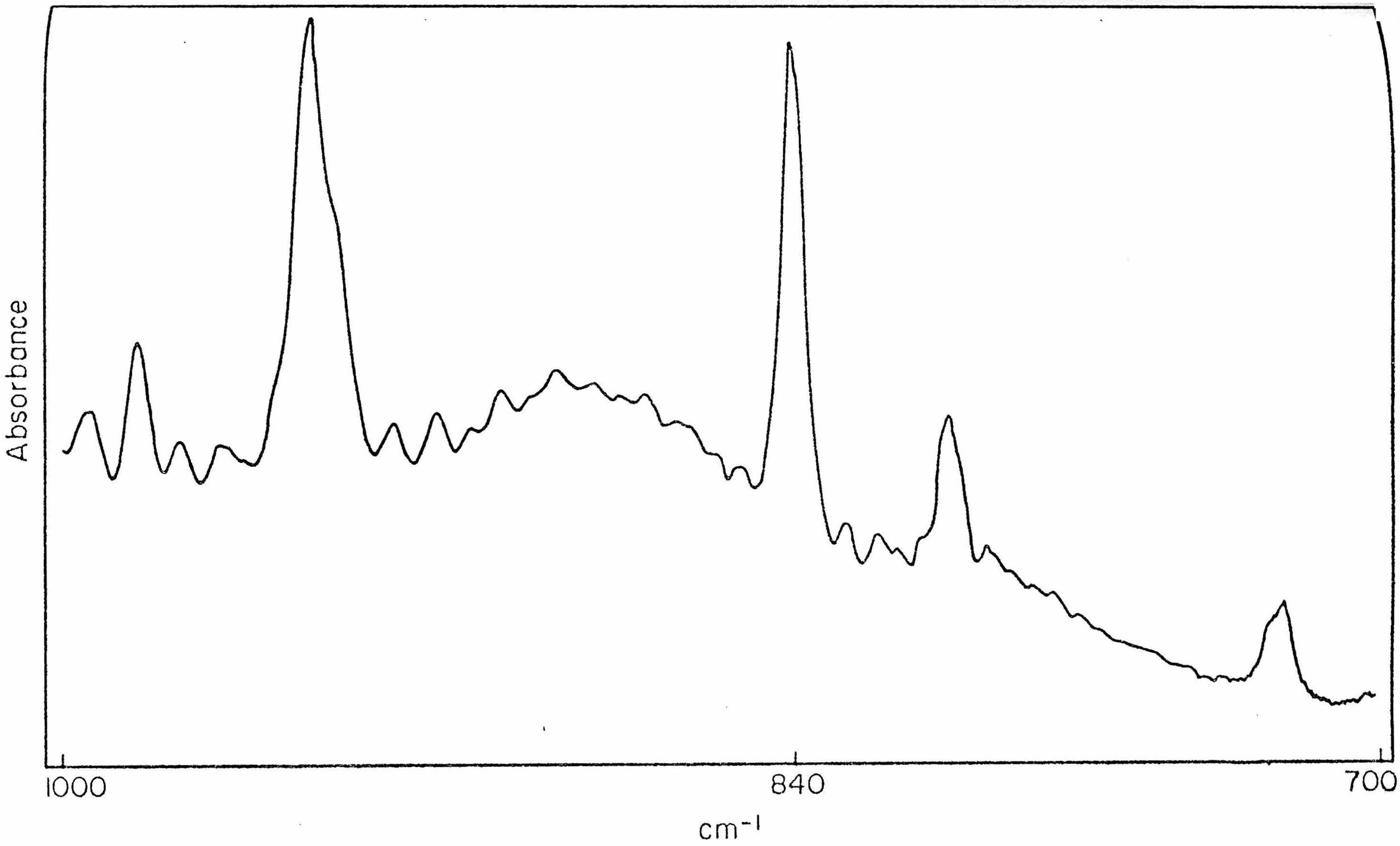


Figure 4. Infrared spectrum of an authentic 84/16 mixture of cis/trans-ethylene-1,2-d_2 (contains ethylene d_1 and d_0).

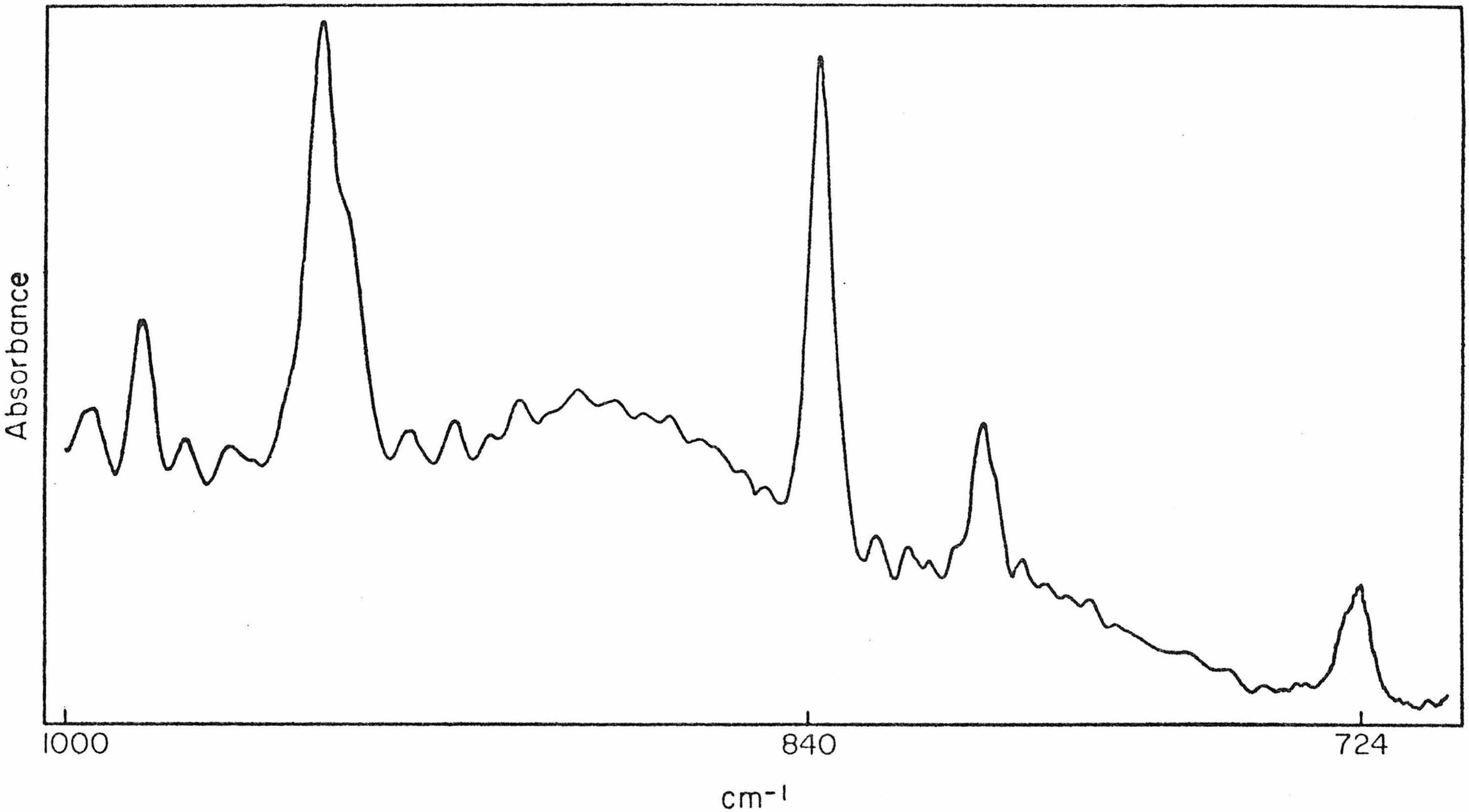


Figure 5. Infrared spectrum of a 79/21 mixture of cis/trans-ethylene-1,2-d_2.

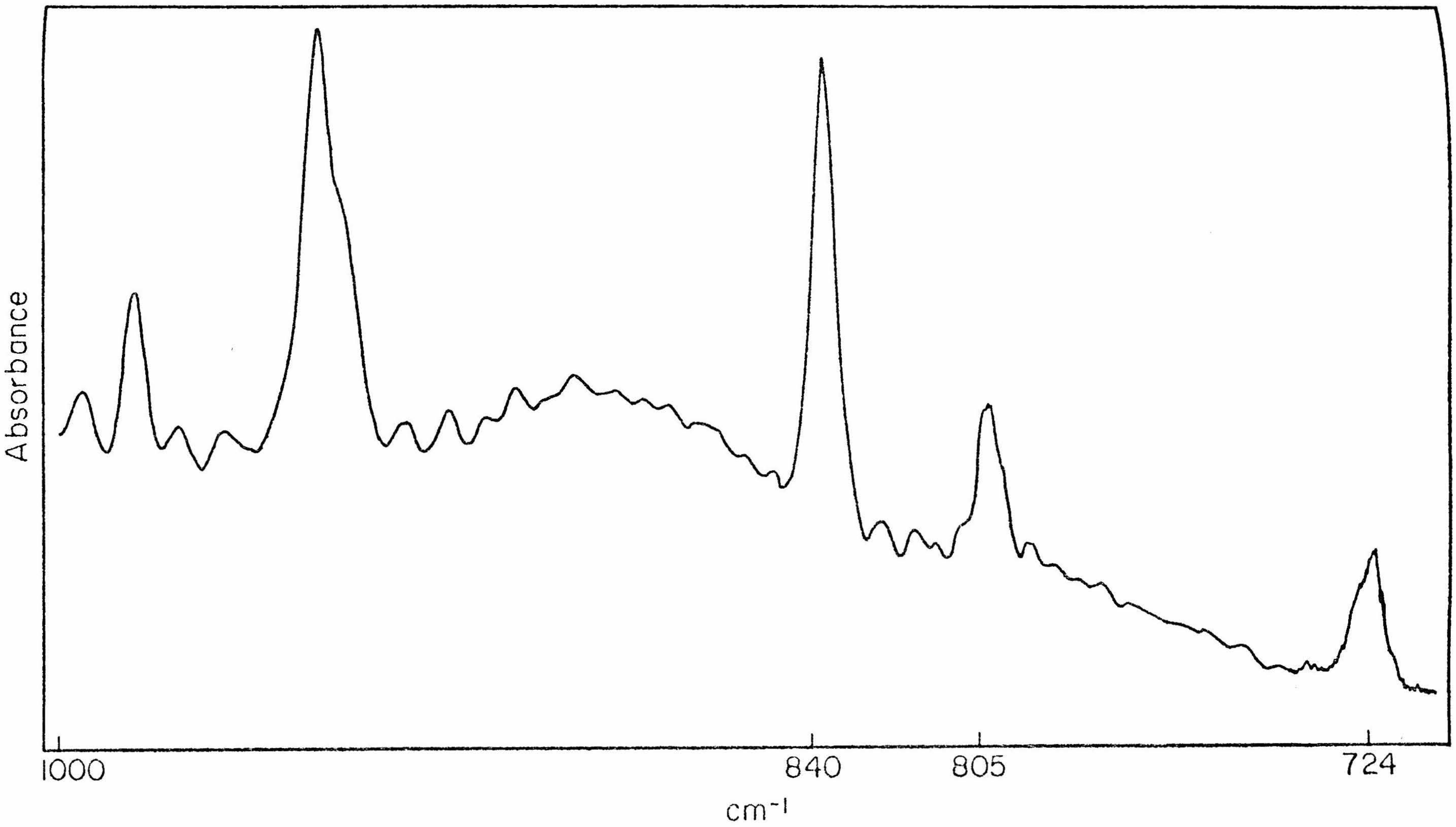


Figure 6. Infrared spectrum of a 74/26 mixture of <u>cis</u>/<u>trans</u>-ethylene-d_2.

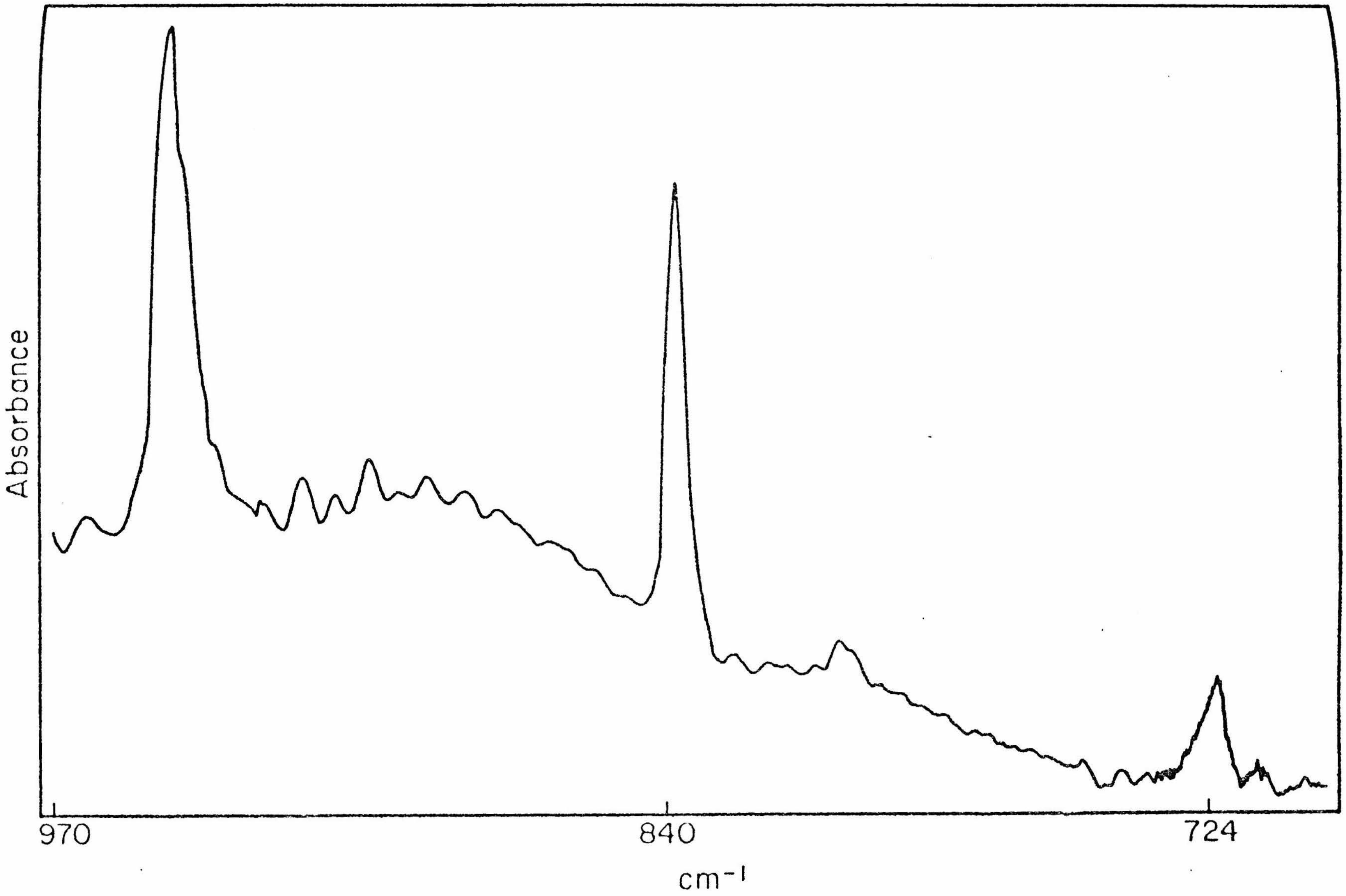


Figure 7. Infrared spectrum of the ethylene products from the pyrolysis of 6.

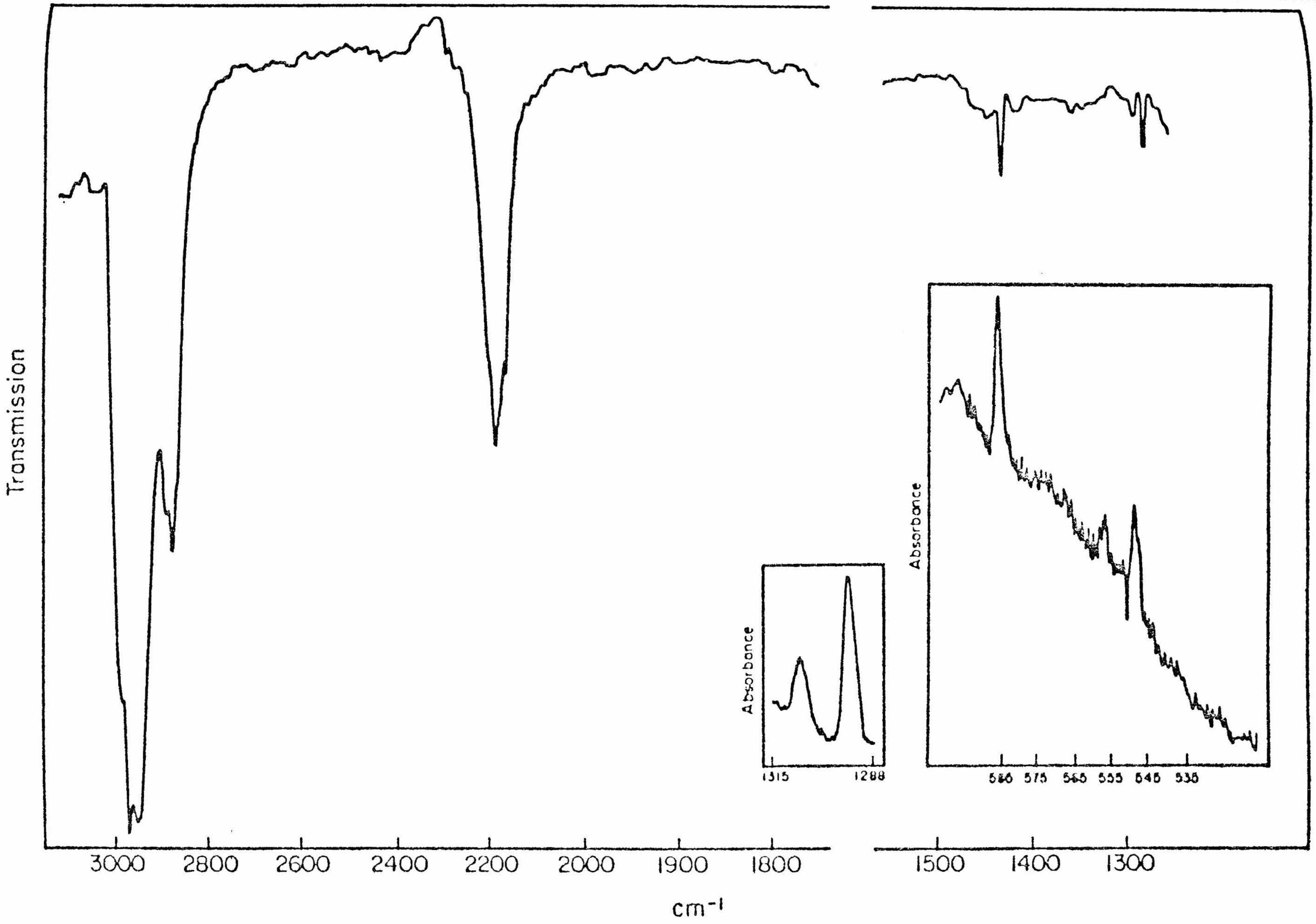


Figure 9. Infrared spectrum of <u>trans</u>-cyclobutane-1,2-d_2.

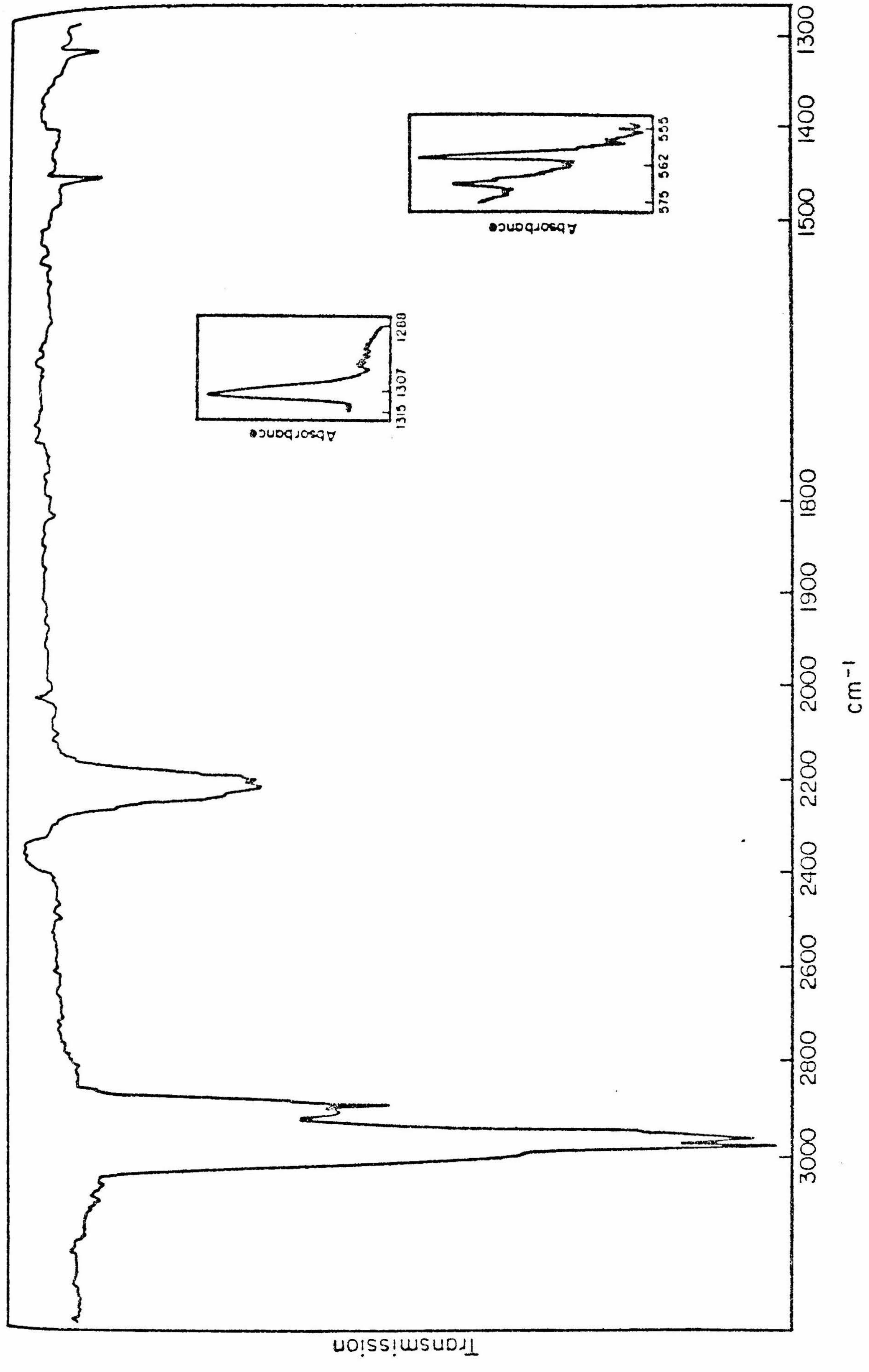


Figure 8. Infrared spectrum of *cis*-cyclobutane-1,2-d_2.

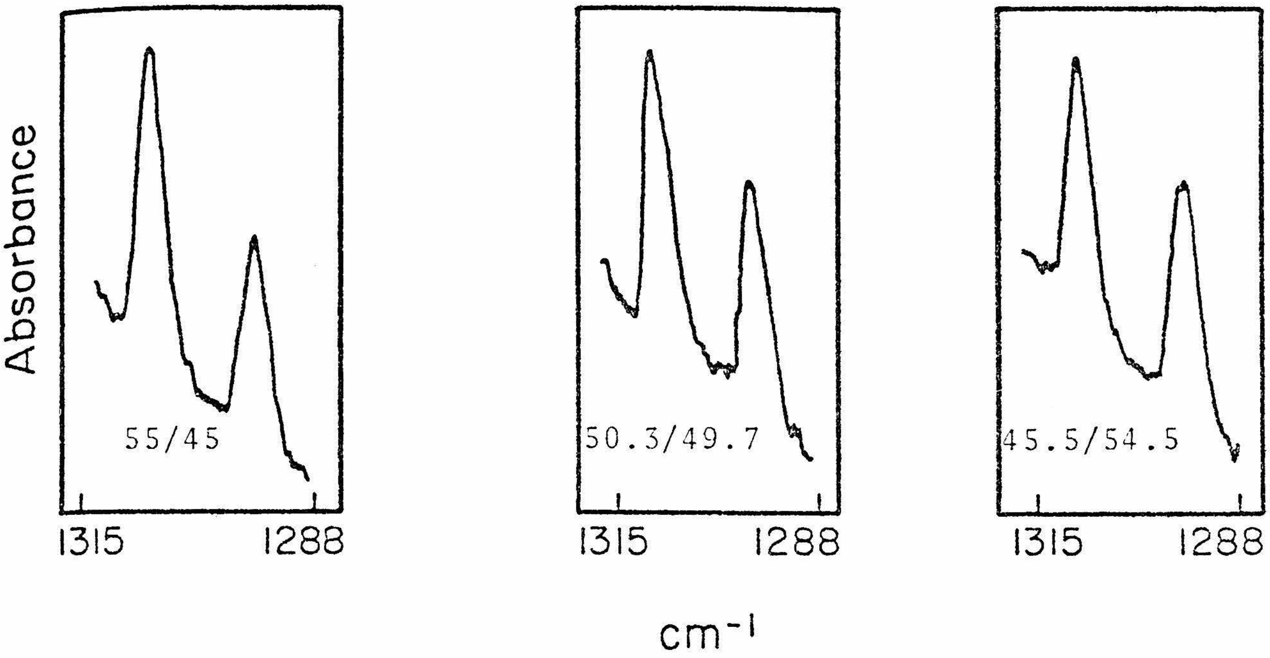


Figure 10. Infrared spectra of authentic mixtures of cis- and trans-cyclobutane-1,2-d_2.

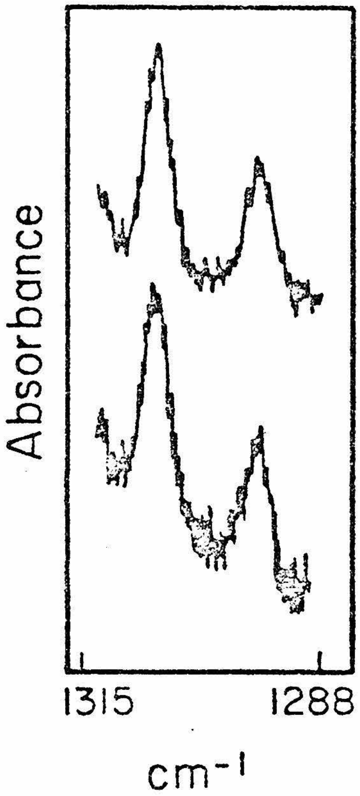


Figure 11. Infrared spectra of the cyclobutane products from the pyrolysis of 6.

Figures 8 and 9 are spectra of isomerically pure samples of cis- and trans-cyclobutane-1,2-d_2. Figure 10 shows the spectra of authentic 55/45, 50.3/49.7 and 45.5/54.5 mixtures of cis- and trans-cyclobutane-1,2-d . Figure 11 shows the spectra of the cyclbutane product from the pyrolysis of 6.

Error Analysis

The determination of and error analyses for the various ratios presented in this paper are given below. The cis/trans-1,2-cyclobutane-d_2 ratio was estimated as follows: The nine data points for the ratio of the 1307 cm^{-1} absorbance to the 1294 cm^{-1} absorbance for the three different relative concentrations of authentic cis/trans-1,2-cyclobutane-d_2 mixtures were used to define a line (absorbance is linear with respect to concentration), and the standard deviation for the slope of the line was set according to the method described by Peters, Hayes, and Heiftje.[27] That is $Y = bX + a$ where Y is the observed peak height ratio, b is the slope of the line, a is the Y intercept, and X is the corresponding cis/trans--cyclobutane-d_2 ratio. The following equations were used in which X and Y are the values described above and n is the number of X, Y data points (see Table 5).

$$\text{slope} = b = \frac{\Sigma UV}{\Sigma U^2}$$

where

$$\Sigma UV = \Sigma XY - \Sigma X \Sigma Y/n$$

$$\Sigma U^2 = \Sigma X^2 - [(\Sigma X)^2/n]$$

$$\text{Y intercept} = a = \frac{1}{n}[\Sigma Y - b\Sigma X]$$

The standard deviation in b is given by

$$\left(\frac{\Sigma V^2 - b^2 \Sigma U^2}{n - 2}\right)/\Sigma U^2$$

where

$$\Sigma V^2 = \Sigma Y^2 - [(\Sigma Y)^2/n]$$

The equation was found to be $Y = 1.03\ x + 0.201$ with standard deviation in the slope of ± 0.02. The 1307 cm^{-1}/1294 cm^{-1} peak height ratio (Y) from the pyrolyses of cis-3,4-tetrahydropyridazine-d_2 was substituted into the equation and the cis/trans-1,2-cyclobutane-d_2 ratio (X) could be calculated.

$$1.51 \pm 0.06 = (1.03 \pm 0.02)X + 0.20$$

or

$$\frac{1.31 \pm 0.06}{1.03 \pm 0.02} = 1.27 \pm 0.06$$

$$(\%\ \text{error in quotient} = [\Sigma(\%\ \text{error}_i)^2]^{1/2}$$

Therefore, cis/trans-cyclobutane-1,2-d_2 = (56±1)/(44±1). Because of uncertainties in the isotopic purities of the authentic samples (± 1% - see Experimental Section) the value (56±2)/(44±2) will be used to compute errors. (The pressure gauge errors in measuring the authentic mixtures are small and are ignored.)

The value and standard deviation of the <u>cis</u>/<u>trans</u>-ethylene-1,2-d_2 ratio was 80.6 ± 1/19.4 ± 1 (Table 6). Also, 2 ethylene/cyclobutane (fragmentation/closure) = 83.2 ± 0.5/16.8 ± 0.5 (Table 4). From these values, the relative amounts of the four deuterated products and their standard deviations can be calculated. (For addition and subtraction standard deviation of the sum or different = $[\sum_{i=1}^{N} \text{error}_i^2]^{1/2}$ where error_i is the error in term i. For multiplication and division, the percent error in the product of quotient = $[\sum_{i=1}^{N} (\%\ \text{error}_i)^2]^{1/2}$ where % error_i is the percent error in term i.

<u>cis</u>-ethylene-1,2-d_2 = (83.2±0.5)(80.6±1) = (67.1±0.9)%

<u>trans</u>-ethylene-1,2-d_2 = (83.2±0.5)(19.4±1) = (16.1±0.8)%

<u>cis</u>-cyclobutane-1,2-d_2 = (16.8±0.5)(44 ±2) = (7.4±0.4)%

<u>trans</u>-cyclobutane-1,2-d_2 = (16.8±0.5)(56 ±2) = (9.4±0.4)%

For

$$\frac{k_{\text{cleavage}}}{k_{\text{closure}}} = \frac{\underline{\text{trans}}\text{-ethylene-1,2-}d_2}{\underline{\text{trans}}\text{-cyclobutane-1,2-}d_2} = \frac{16.1 \pm 0.8}{7.4 \pm 0.4} = 2.2 \pm 0.2$$

For

$$\frac{k_{\text{rotation}}}{k_{\text{closure}}} = \frac{R_1 + 1}{R_2 R_1 - 1} = \frac{1}{R_2 - 1} + \frac{1}{R_1(R_2 - 1)}$$

where

$$R_1 = \frac{k(\text{closure})}{k(\text{cleavage})} = 0.459 \pm 0.34$$

$$R_2 = \frac{\underline{\text{cis}}\text{-cyclobutane-1,2-d}_2}{\underline{\text{trans}}\text{-cyclobutane-1,2-d}_2} = 1.27 \pm 0.06$$

or

$$\frac{k_{\text{rotation}}}{k_{\text{closure}}} = 12 \pm 3$$

Controls

(a) The hydrazone and the hydrazine 24 afforded ethylene and cyclobutane under identical pyrolysis conditions in less than 1% yield.

(b) trans-Ethylene-1,2-d_2 was shown to be stable under the pyrolysis conditions.

(c) Cyclobutane gave no ethylene under the pyrolysis conditions.

(d) As expected, the presence of ethylene-d_0 in the pyrolysis product mixture, was shown not to affect the 842 cm^{-1} to 724 cm^{-1} peak height ratio, by adding nearly equivalent amounts of ethylene to the authentic mixtures.

(e) Surface effects were checked by repeating the pyrolyses with a tube filled with glass chips. None were found. Also, pressure effects were absent since 150 ul injections (ca. 300 Torr) gave the same ethylene/cyclobutane product ratio as 10 ul injections (ca. 20 Torr).

(f) The ratio of azo compound to an internal standard (ethyl ether) in benzene-d_6 was determined by NMR. After pyrolysis, the ratio of hydrocarbon products/ethyl ether afforded a rough estimate of mass balance. Most of the azo compound 6 decomposed to ethylene and cyclobutane. The rest rearranged irreversibly to the corresponding hydrazone.

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9) The headings for this table are reversed in reference 5e. The table is correct as it appears here.

10) For an alternate synthesis and thermolysis of *cis*- and *trans*-cyclobutane-1,2-d_2, see reference 3j.

11) This reaction has been shown to be 95% stereospecific inversion for secondary centers, i.e., *threo*-3-methyl-1,4-pentanediyl-1,4-dimethanesulfonate affords dimethyl *cis*-3,4-dimethyltetrahydropyridazine-1,2-dicarboxylate and erythro-dimethanesulfonate affords *trans*-3,4-disubstituted diurethanes.[5e]

12) Perkin-Elmer Model 180 infrared spectrophotometer. We thank Dr. George Rossman, Division of Geological and Planetary Sciences, California Institute of Technology for allowing us to use this instrument.

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CHAPTER II

Thermal Decomposition of Cyclic Azo Compounds by Photoelectron Spectroscopy. Implications for the Fate of Energy Released on Fragmentation

INTRODUCTION

In the process of studying reaction mechanisms, chemists have employed many techniques to elucidate the details of molecular reorganizations. Among the most powerful and widely used techniques are kinetic and stereochemical studies. With the advance of new physical methods, the organic chemist has utilized new techniques for the direct observation of previously postulated transient high energy species. Infrared, nuclear magnetic resonance, Raman, and electron spin resonance spectroscopy have been used in this manner.[1] Recently, photoelectron spectroscopy has emerged as a powerful tool in chemistry.[2] From the correct interpretation of the PE spectrum of a molecule, the molecular orbital energies (and the electronic structure) of the molecule can be determined.

In photoelectron spectroscopy, molecules in the gas phase are irradiated with monochromatic light (usually the Helium I line at 21.21 eV). Electrons are ejected from the molecule due to the impinging beam and are analyzed yielding a spectrum of relative intensity versus energy. Because the energy of He I light and the energy of the expelled electrons are known, the ionization energies for the electrons can be calculated. Koopman's theorem states that the difference between the energy put into the molecule and the energy of the expelled electron is directly related to the energy of the molecular orbital from which the electron came. Therefore, one would expect to see a series of bands in the PE spectrum corresponding to electrons from specific molecular orbitals. (The lower the molecular orbital is in energy, the lower in energy is the expelled electron because of its higher ionization potential.) The shape of the band depends on the Franck-Condon overlap of the vibrational energy level of the original and final electronic state, so information can be obtained about the type of orbital from which an electron came.

A photoelectron spectrometer, equipped with a heated inlet system to pyrolyze molecules near the Helium I beam, could be used as another tool for directly obtaining the spectra of transient species. At the California Institute of Technology, in J. L. Beauchamp's research group, Frances Houle has equipped a photoelectron spectrometer with a heated inlet system.[3] Molecules are pyrolyzed near the photon beam so that species with lifetimes of $\sim$ 1 msec at pressures of 50-100 mTorr are readily observable. The photoelectron spectra of such transient species as alkyl radicals from the pyrolysis of alkyl nitrites have been recorded.[3]

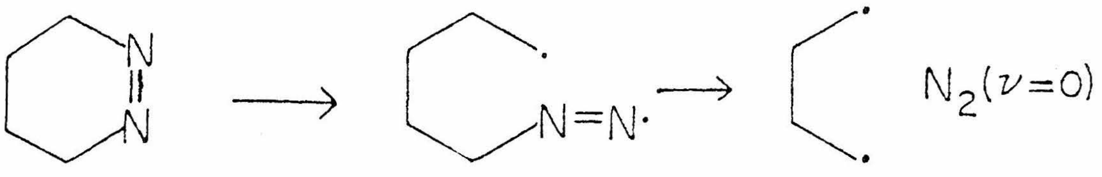
The mechanism of 1,2-diazene cleavage is poorly understood. The question arises whether the process involves (a) a two step cleavage of the nitrogen-carbon bonds or (b) whether the bond break simultaneously

$$\text{a)}\quad R\text{-}N{=}N\text{-}R' \longrightarrow R\cdot + \underset{\underline{1}}{\cdot N{=}N\text{-}R'} \longrightarrow R\cdot + N_2 + R'\cdot$$

$$\text{b)}\quad R\text{-}N{=}N\text{-}R' \longrightarrow R\cdot \; N_2 \; R'\cdot$$

For acyclic azo compounds, it appears that the mechanism depends on the R groups. If one R group forms a more stable radical than the other, one bond (two step) cleavage occurs.[4] In the thermal decomposition of unsymmetric acyclic azo compounds, evidence for the diazenyl radical (<u>1</u>) has been reported by N. Porter using CIDNP and trapping studies.[5] However, for symmetrical and cyclic azo compounds, neither mechanism has been excluded.

The two limiting mechanisms for cyclic azo decomposition involve either a diazenyl radical intermediate <u>2</u> (stepwise cleavage) or a symmetric transition state <u>3</u> (concerted cleavage of both C-N bonds). S. H. Bauer has suggested that if bond breaking were concerted, the organic and nitrogen fragments would be poorly coupled and the excess energy released during the reaction would not be randomized throughout the molecule.[6] Furthermore,



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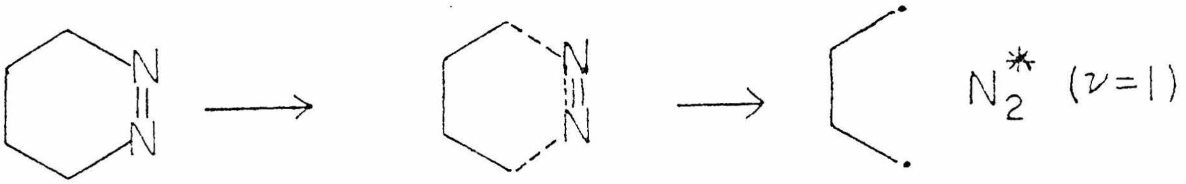

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since the structure of the free nitrogen (N≡N) differs from its structure in the parent azo species (-N=N-), the nitrogen may trap a high proportion of the available energy of the transition state in the form of geometric distortion. If the cleavage is stepwise, however, excess energy can flow into the organic framework by delocalizing throughout all of the degrees of freedom in the diazenyl radical. Perhaps, in the concerted mechanism, the nitrogen is expelled in a vibrationally "hot" state while in the stepwise mechanism it is "cold". A study of a series of

1,2-diazene decompositions in a heated inlet of a PE spectrometer may then reveal some subtle details about this reaction mechanism.

Three questions arise. (1) Is there enough energy available for nitrogen to be expelled in a vibrationally excited state? (2) Is vibrationally excited nitrogen long-lived enough to be observed? (3) Can photoelectron spectroscopy detect a vibrationally excited molecule of nitrogen from a thermal fragmentation of 1,2-diazenes?

The first question will be applied to the pyrolysis of 4, an azo compound which has recently been prepared[7] and thermally decomposed.[8] The reaction pathway is summarized in Fig. 1. The transition state is 81.8 kcal mol^{-1} above the products.[8] The energy between the first and ground vibrational states of nitrogen is 6.5 kcal mol^{-1}.[9] Thus, if the nitrogen does carry a high proportion of the available energy of the transition state upon dissociation, it can become vibrationally excited.

At 0.5 Torr, vibrationally excited nitrogen has a lifetime of 1 msec.[10] As stated previously, a species formed in the heated inlet of the photoelectron spectrometer with such a lifetime should be easily observed. It is not expected that the vibrational energy of the nitrogen fragment will be significantly removed by the up to 100 collisions it suffers before being analyzed.[11]

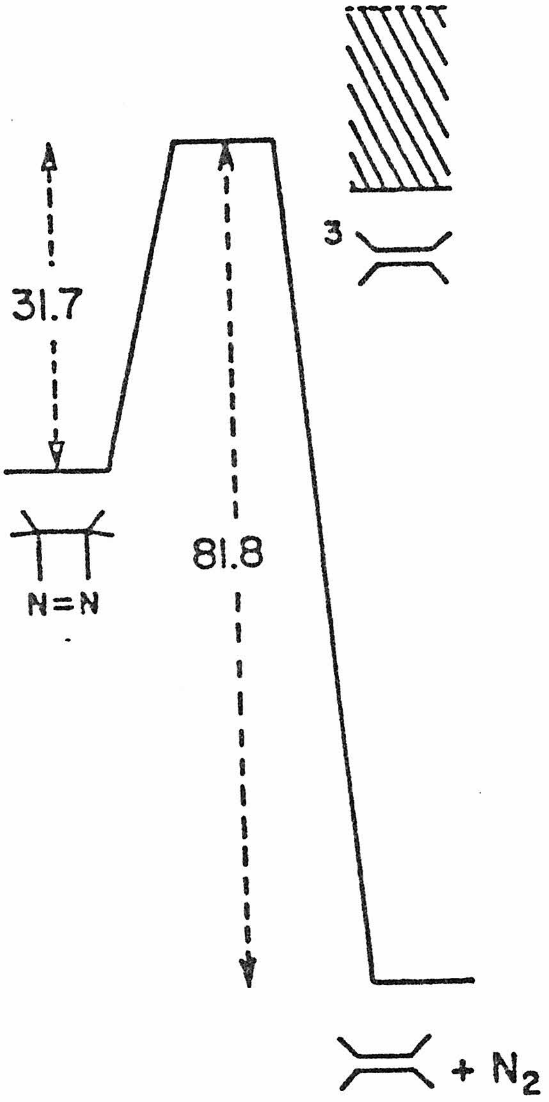


Figure 1. Energy surface for the pyrolysis of 4 (values are in kcal mol^{-1}).

The third requirement, concerning the detectability of a vibrationally excited molecule of nitrogen by photoelectron spectroscopy, has been met. Figure 2 illustrates how a vibrationally excited molecule can be detected.

Because most molecules are in the ground vibrational state at the temperatures in question, a spectrum from the above system will show a band with fine structure due to the difference in the v_0', v_1', and v_2' energies. (Before ionization, all molecules are in the v_0'' level of the E_1 electronic state. The intensity of the lines depends on the vibrational Franck-Condon overlap of the v_1' states with the v_0'' state.) The lowest energy (adiabatic) transition between the electronic states (yielding the free electron with the highest energy) is the $v_0'' \rightarrow v_0'$ transition.

Note, however, that if a molecule is in a vibrationally excited state (v_1''), there will be a distinct lower ionization potential band from the $v_1'' \rightarrow v_0'$ transition. This is actually not the only difference. Because of the anharmonicity of the "harmonic" oscillator model, the vibrational levels are not evenly spaced, so, for example, the $v_1'' \rightarrow v_2'$ transition will not be the same as the $v_0'' \rightarrow v_1'$ transition, though they will be close.

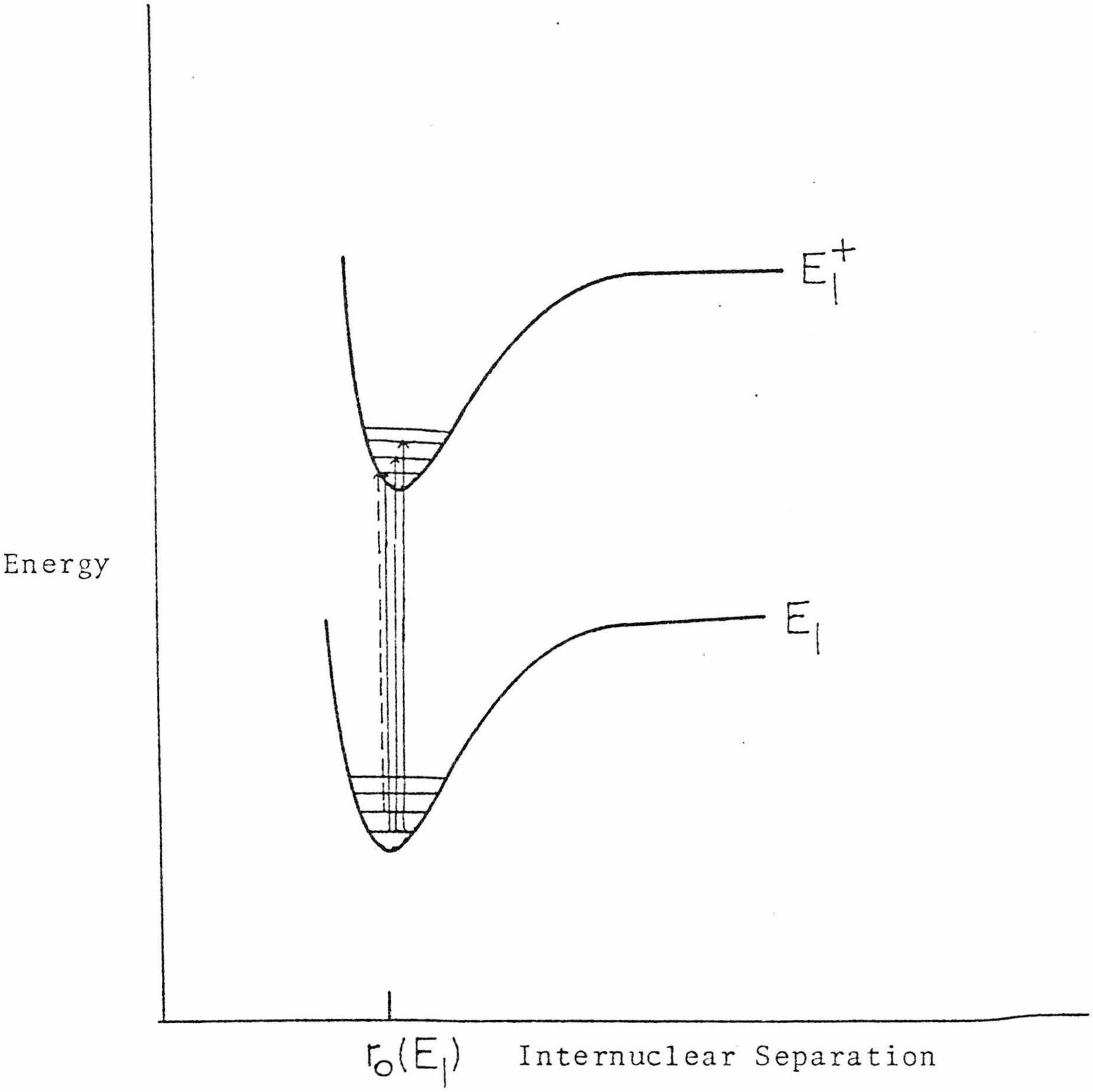


Figure 2. Energy differences (arrows) between the vibrational states of the ground electronic state of a compound (E_1) and an electronic state of the compound's cation (E_1^+).

The photoelectron spectra of nitrogen and vibrationally hot nitrogen (from a hot discharge) have been recorded (see Fig. 3).[12] Table I lists some ionization potentials of nitrogen (v'' = 0) and nitrogen (v'' = 1).

Table 1

PES Bands From N_2

N_2 Transition	Band (Symmetry Designation)[a]		
	$X^2\Sigma_g^+$	$A^2\bar{\Lambda}_u$	$B^2\Sigma_u^+$
v'' = 0 → v' = 0	15.57[b]	16.69	18.75
v'' = 0 → v' = 1	15.84	16.91	19.09
v'' = 1 → v' = 0	15.29	16.46	18.54

[a] This represents the electronic state to which v' belongs in the transition. These bands correspond to ionizations from the three highest occupied molecular orbitals of nitrogen.

[b] Ionization potential/eV.

Therefore, it is evident that photoelectron spectroscopy may yield qualitative information about presence of vibrational excitation in the nascent products of azo decompositions. This information can be used to elucidate the mechanism of azo decomposition. In addition, it would be an attempt to probe directly the energy of the nascent products as they emerge from a transition state or intermediate in order to provide insight on the structure of that species.

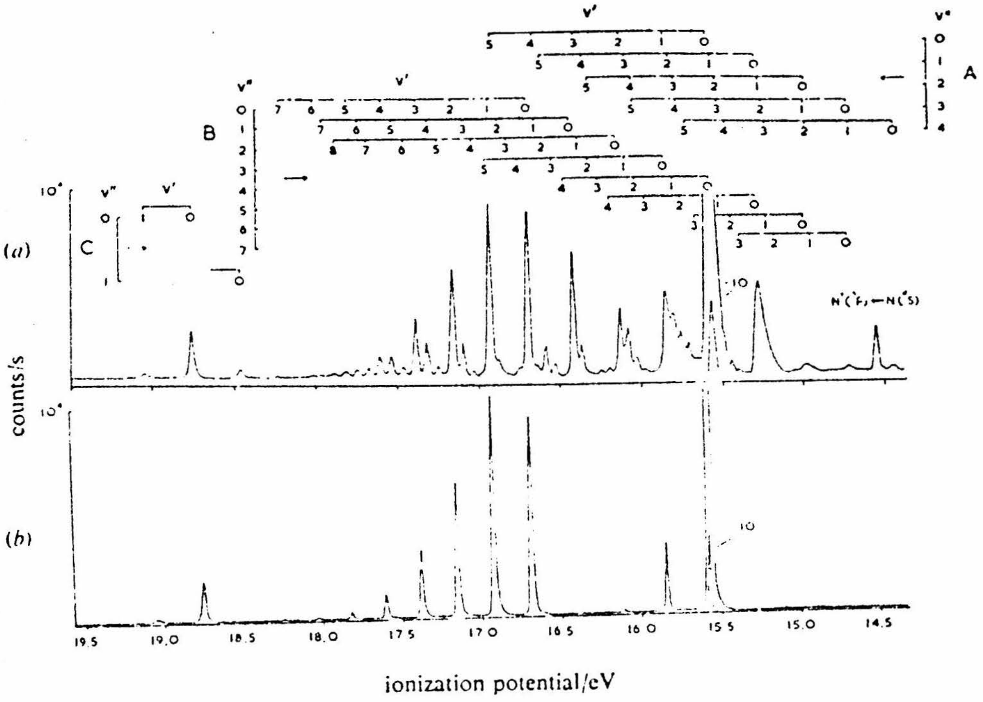
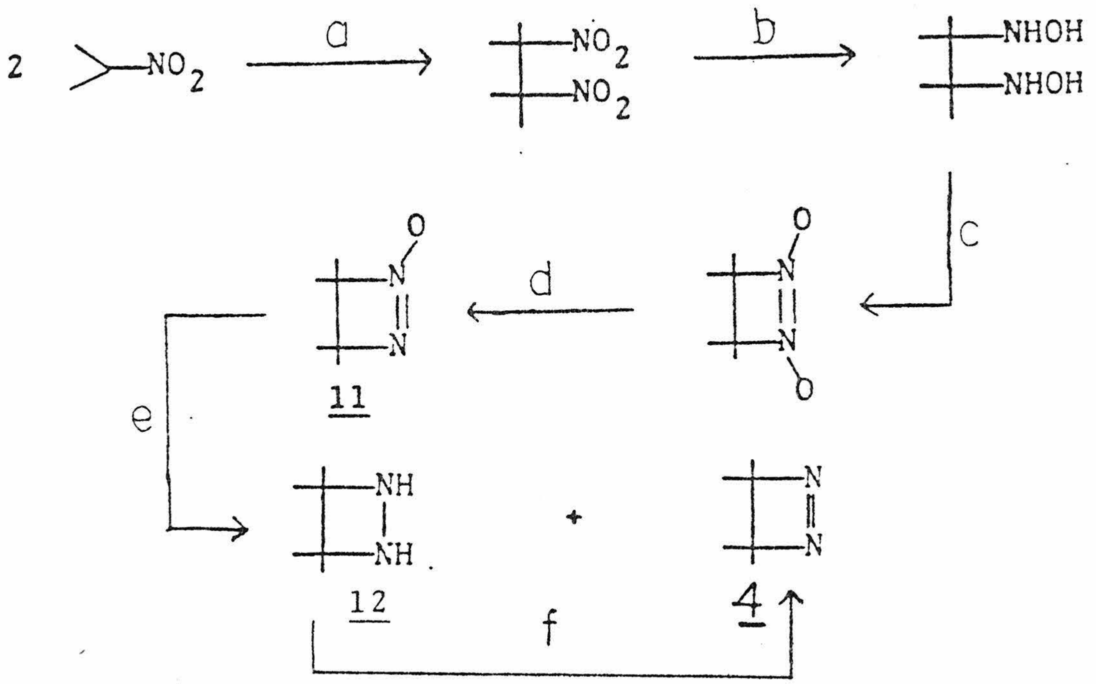


Figure 3. Photoelectron spectrum of (a) discharged nitrogen, (b) undischarged nitrogen, observed with Helium I radiation. (The transitions are from the v" of N_2 to the v' of N_2^+. Note the v" = 1 to v' = 0 transition of 15.3 eV in (a).) Figure is from reference 12.

RESULTS AND DISCUSSION

With some slight modifications, 3,3,4,4-tetramethyl-Δ^1-1,2-diazetine (4) was synthesized and purified using the method of Green (see Scheme I and experimental section).[7] The photoelectron spectrum of 4 was recorded and

Scheme I



(a) Li/MeOH, CCl_4, (b) Zn/EtOH, HCl, (c) Br_2/H_2O, (d) $Si_2Cl_6/CHCl_3$, (e) $LiAlH_4$/ether, (f) Ag_2O/MeOH.

agreed with a spectrum that eventually appeared in the literature (Fig. 4).[13] The photoelectron spectroscopy was conducted by Frances Houle (see Experimental Section).

The pyrolysis spectrum is shown in Fig. 5. As expected from the thermolysis of 4 in solution, the only

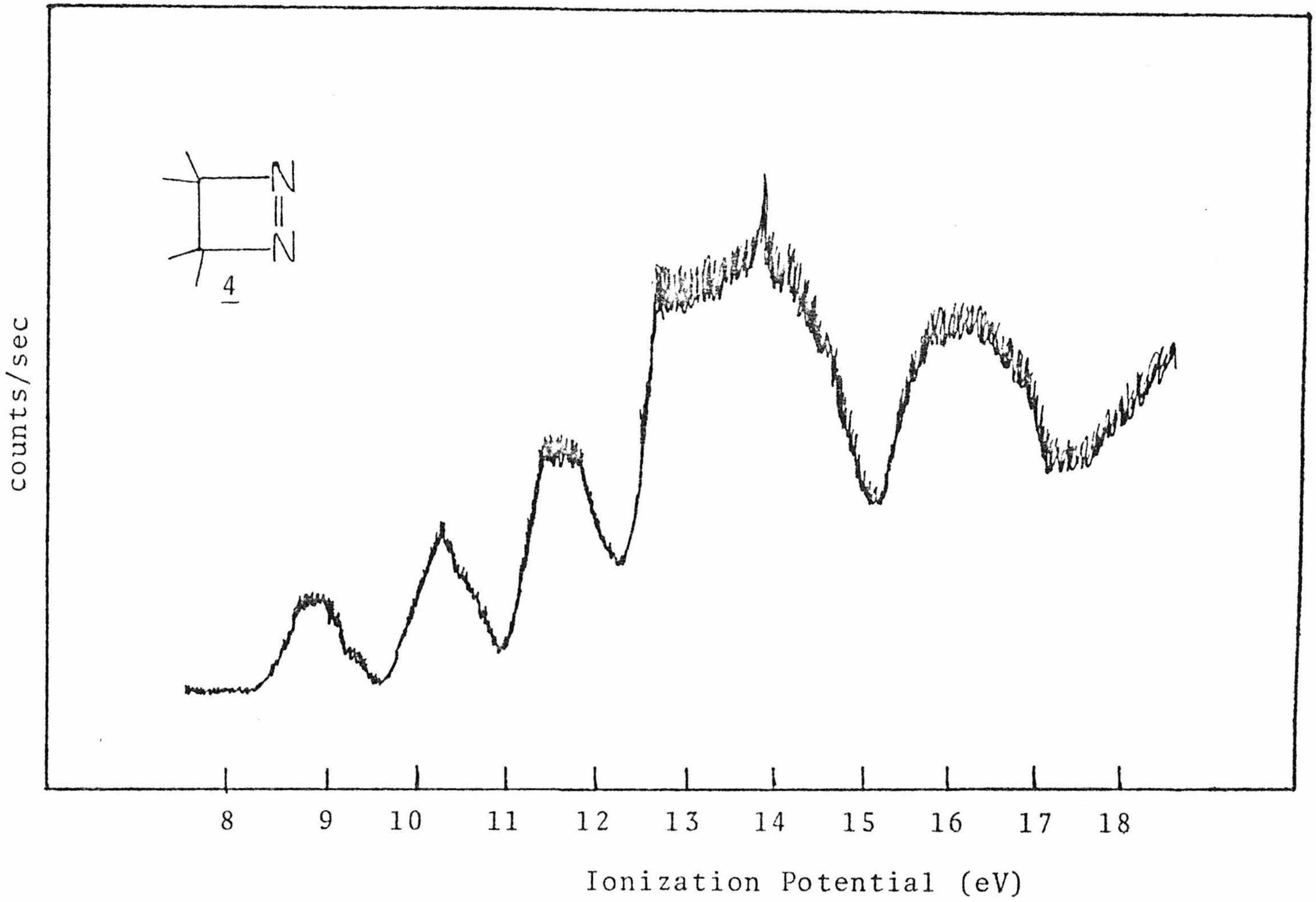


Figure 4. Photoelectron spectrum of 4

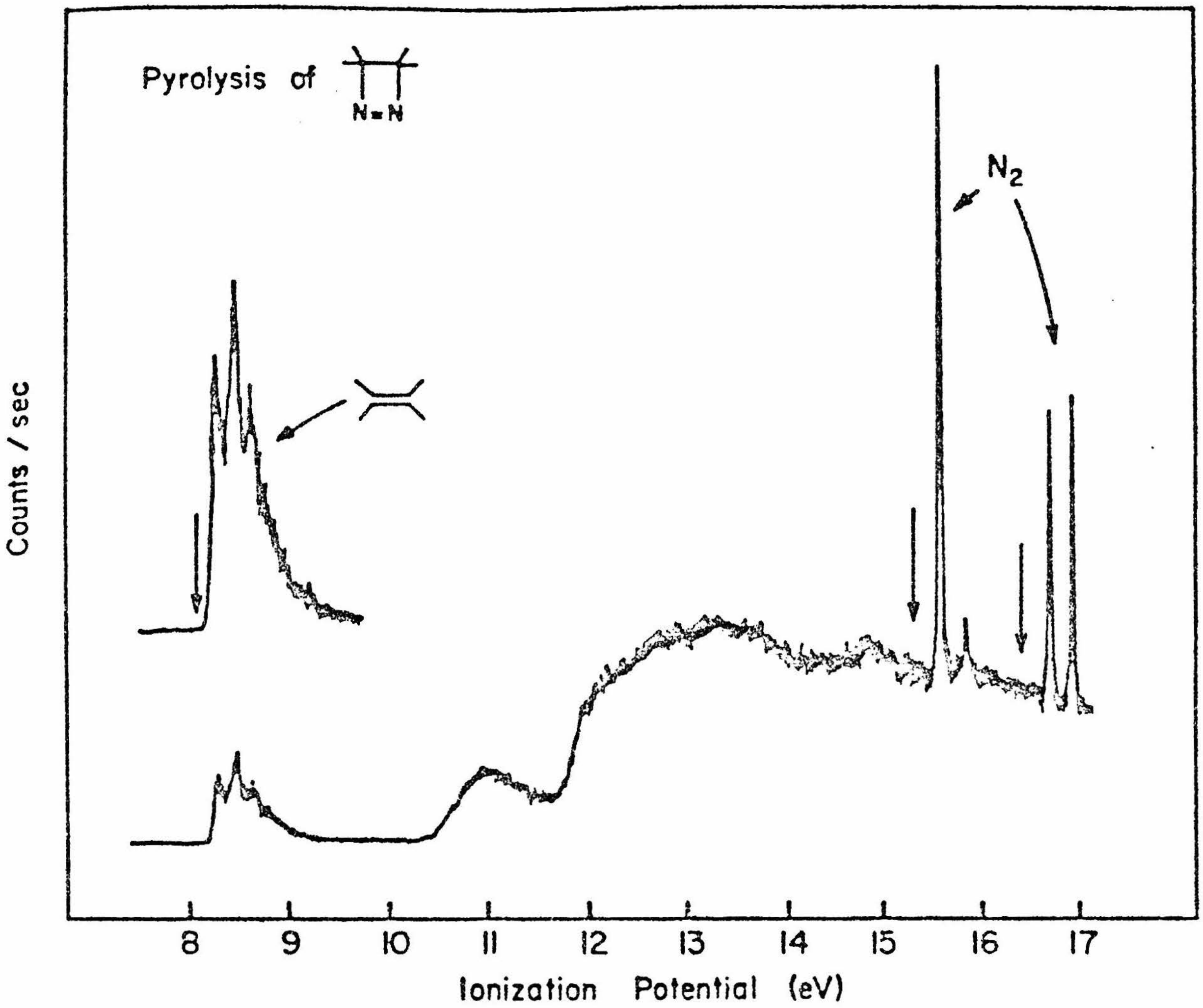


Figure 5. Photoelectron spectrum of the pyrolysis products of 3,3,4,4-tetramethyldiazetine (4). N_2 and 2,3-dimethyl-2-butene are present.

observed products are nitrogen and 2,3-dimethyl-2-butene.[8] Hot bands of either 2,3-dimethyl-2-butene or N_2 should be readily observable if present. These peaks would appear at lower energies than the adiabatic ionization potentials as described previously. For the 2,3-dimethyl-2-butene fragment, this corresponds to a quantum of -C=C- stretching energy (if this bond is excited) or 0.207 eV below the adiabatic ionization potential.[14] For nitrogen, the peak should be 0.28 eV lower (see Table I). The expected locations of hot bands are shown by arrows in Fig. 5, and it is evident that there are no bands visible. (In order to observe a signal from a hot molecule, approximately 5% of the nitrogen would have to be excited - see experimental section.)

Thermochemical measurements have shown that 81.8 kcal mol^{-1} are available to the products from the pyrolysis of 4 (Fig. 1).[8] The disposal of this considerable exothermicity into the products can be detected in the photoelectron spectrum if either the olefin or nitrogen fragment is vibrationally excited or if 2,3-dimethyl-2-butene becomes electronically excited. The triplet energy of 2-butene is 80 kcal mol^{-1}, so formally there is enough energy available to reach this state.

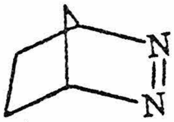
The absence of any hot bands can be explained as follows. If nitrogen extrusion were concerted, the bond length in the nascent fragment would be ∿ 1.24 Å (azo) compared to 1.09 Å in the N=N triple bond.[15] It has been estimated that this "stretched" nitrogen would contain ∿ 4 quanta of vibrational energy or 26.7 kcal mol^{-1}.[16] This suggests that the nitrogen is formed from an undistorted precursor, perhaps the diazenyl radical, and the energy released from the transition state is randomized throughout the products.

Is energy randomization in the products consistent with the observed pyrolysis spectrum? Frances Houle has calculated the percent of vibrationally excited 2,3-dimethyl-2-butene and nitrogen expected from the pyrolysis of 4 if the energy is randomized throughout the vibrational modes of the molecule.[17] The 82 kcal mol^{-1} internal energy corresponds to a vibrational temperature of ∿ 800°, and at this temperature, 4% of the N_2 stretch in nitrogen and 11% of the C=C stretch in the olefin are expected to be in the first vibrationally excited state. These values are upper limits since wall collisions, rotations, and translation may remove some of the vibrational energy initially present in the fragments.[17] Therefore, it is reasonable to expect no visible hot bands in the spectrum of the products from a vibrationally equilibrated intermediate from the pyrolysis of 4.

The possibility of forming triplet 2,3-dimethyl-2-butene is remote. Although the adiabatic transition to the triplet olefin requires ∿ 76 kcal mol^{-1}, the vertical (most probable) transition requires ∿ 94.5 kcal mol^{-1}, considerably more than the 82 kcal mol^{-1} available.[18] Furthermore, the pyrolysis of *meso*- and *dl*-3,4-diethyl-3,4-dimethyldiazentine by White and Green yielded olefin products in which no rotation was observed.[19] A triplet olefin would be expected to undergo some stereorandomization. No triplet 2,3-dimethyl-2-butene was observed in the photoelectron spectrum of the pyrolysis of 4 (triplet 2-butene lifetimes are on the order of 1 msec).[20]

Kropp has photolyzed 2,3-dimethyl-2-butene in methanol and found methyl ether products resulting from the reaction of an excited state of the olefin with the solvent.[21] The amount of excess energy in the olefin, postulated to be in an excited Rydberg electronic state, is estimated to be *ca.* 120 kcal mol^{-1}.[21] In order to test the possibility that the pyrolysis of 4 produced 2,3-dimethyl-2-butene in the Rydberg state, 4 was heated to 150° for 23 hr in methanol in a sealed tube. The reaction products were analyzed by vapor phase chromatography. The ethers expected from the excited olefin were not observed, and only 2,3-dimethyl-2-butene formed (see experimental section). This experiment was conducted before the thermochemical measurements of 4 were conducted.[8] The results of this thermolysis are consistent with the fact that only 82 kcal mol^{-1} are available to the olefin compared to the *ca.* 120 kcal mol^{-1} needed to reach a Rydberg state.

D. M. Ingle and F. Houle investigated the pyrolysis of 2,3-diazabicyclo[2.2.1]heptane and 3,4-diaza-exo-tricyclo-[4.2.1.0^{2,5}]non-3-ene (5 and 6, respectively) using photoelectron spectroscopy.[3] No vibrationally excited fragments were detected even though the reaction of 6 was exothermic by 83.2 kcal mol^{-1}.



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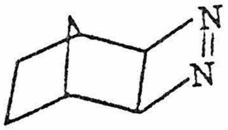

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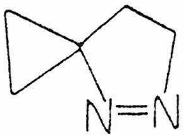
Although the rationalizations for being able to detect the presence of hot nitrogen are sound, it seems essential to perform a control experiment in which a molecule which has independently been shown to produce hot nitrogen is pyrolyzed in the photoelectron spectrometer. Detection of hot nitrogen in this experiment would lend credence to the expectation that photoelectron spectroscopy is capable of such a feat. The pyrolysis of hydrazoic acid has been shown to produce vibrationally excited nitrogen.[22] Population inversions of carbon dioxide were created by the transfer of energy from vibrationally excited nitrogen (from the pyrolysis of HN_3) to CO_2. An attempt by Ingle and Houle to detect and pyrolyze this molecule in the spectrometer failed, perhaps because of induced decomposition.[3] Modifications of the inlet and pyrolysis systems (perhaps by the use of a pyrex lining) could make such experiments possible and should be undertaken.

Assuming that this method of detecting hot nitrogen is valid, a test of a prediction by Shen and Bergman can be made.[23] Compounds 7 and 8 were pyrolyzed. These authors found that in the unsymmetrical azo compound 7, the organic fragment was released as an energetically excited species and underwent further reaction. However, in symmetric 8, the organic fragment did not contain enough excess energy to react further. Bergman postulates that in



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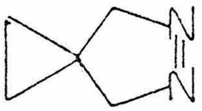

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the symmetric case, the nitrogen is extruded with the simultaneous rupture of both C-N bonds, and, according to Bauer's criterion, contains much of the excess energy of the reaction. For 7, the bond rupture is stepwise and the excess energy can flow into the organic framework. A comparison of the photoelectron spectrum of the nascent nitrogen from the pyrolysis of 7 and 8 could yield some illuminating data, and these experiments are now under consideration.

The photoelectron spectrum of 4 is of interest (Fig. 4). The first three bands of azo photoelectron spectra are due to the antisymmetric (n_-) and symmetric (n_+) combinations of lone pair orbitals on nitrogen and to the

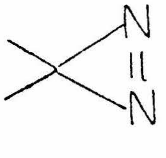
π orbital.[13,24] These occur at 8.75, 10.25, and 11.6 eV respectively. Therefore the splitting between the n orbitals, $\Delta n_{\pm}$, equals 1.5 eV.

Brogli et al., attempted to rationalize the Δn value in terms of the NNC bond angle.[25] MINDO II calculations predict the splitting will be a minimum for NNC angles of *ca*. 100°, and it is postulated that the n_{+} orbital interaction with a low lying N-N σ orbital is angularly dependent. These predictions are borne out as shown in Table 2.

Table 2

$\Delta n_{\pm}$ Values For Cyclic Azo Compounds

Compound	NNC Angle	$\Delta n_{\pm}$ (eV)
3-member ring azo 9	65°	3.55
4-member ring azo 6	95°	1.50
4-member ring azo 4	95°	1.50
5-member ring azo 5	111°	3.10



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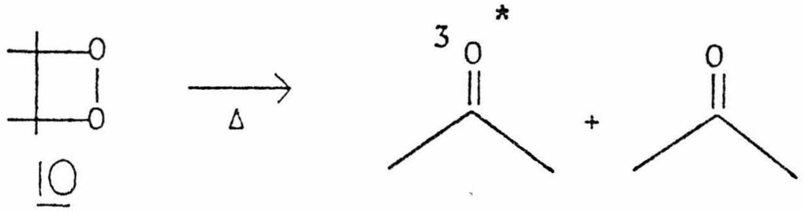
Because of the availability of a photoelectron spectrometer with a heated inlet, tetramethyl dioxetane (10) was synthesized with the hope of directly observing the formation of triplet acetone (Scheme II). Even the photoelectron spectrum of 10 would be of interest.

Scheme II



The mechanism of the decomposition of 10 has been intensively studied.[26] There is sufficient energy to excite one acetone fragment to a triplet or perhaps a singlet state. A thermochemical study of this system reveals similarity to the decomposition of 4 (see Fig. 6).[26]

The lifetime of the triplet is estimated to be 20 usec in solution and may be observable using the heated inlet of the photoelectron spectrometer since triplet acetone has a longer lifetime (on the order of seconds) in the gas phase.[27]

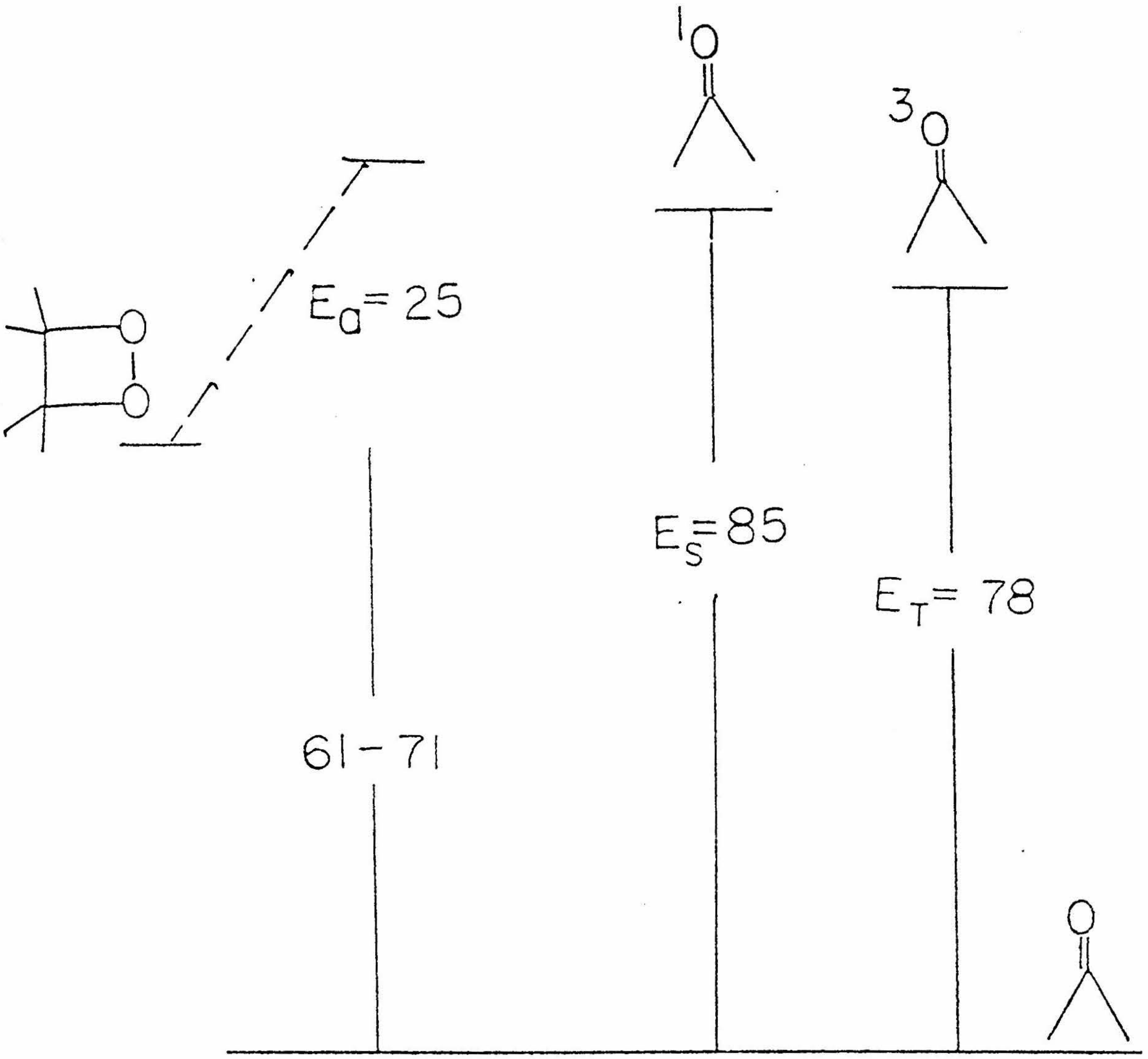
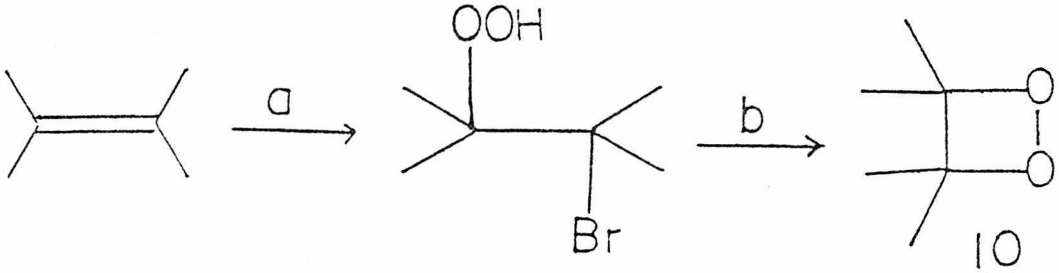


Figure 6. Energetics of the pyrolysis of tetramethyl dioxetane. (Energies are in kcal mol^{-1}.)

The triplet can be recognized by PE spectroscopy because an electron occupies the π^* orbital which is 4.15 eV above the n orbital.[28] Therefore, another band, 4.15 eV lower than the lowest band of acetone should be evident.

Therefore, 10 was synthesized as described by Turro and Schore (see Scheme III).[29] However, not even the photoelectron spectrum of the dioxetane could be obtained due to decomposition to acetone, perhaps catalyzed by the metal in the inlet system. The construction of a glass-lined inlet and pyrolysis system may alleviate this problem.

Scheme III



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(a) Hydrogen peroxide, 1,3-dibromo-5,5-dimethylhydantoin,
(b) Silver acetate.

EXPERIMENTAL SECTION

3,3,4,4-Tetramethyl diazetine N-oxide (11) was synthesized as described by Greene.[7]

3,3,4,4-Tetramethyl Δ'-1,2-diazetine (4). 1.2g (6.032 moles) of lithium aluminum hydride was added to a vigorously stirred solution of 0.5g (0.004 moles) of 11 in 70 ml of anhydrous ether. The mixture was allowed to reflux for 30 min, cooled in ice, and the lithium aluminum hydride was quenched by the dropwise addition of 1.2 ml water, 1.2 ml of 15% sodium hydroxide solution, and 3.6 ml of water. A white granular precipitate formed. This was filtered, dried (K_2CO_3) and concentrated. The oily residue was dissolved in a small amount of ether and purified by preparative gas chromatography (25% UCW 98, 70° glass). The first eluted compound (relative retention time = 1.0) (white solid 4) NMR ($CDCl_3$) δ 1.25 (s), UV (cyclohexane) λ (relative intensity): 356 nm (0.75), 347.5 (1), 340 (0.91), 333 (0.67), 325 (0.42); mass spectrum m/e (relative intensity) 84 (40), 69 (100), 41 (100).

The second eluted isomer (relative retention time = 1.4) (12) NMR ($CDCl_3$) δ 1.10 (s, 7), 2.1 (b, 1) (upon addition of D_2O to the solution, the peak at δ 2.1 disappeared). Presumably 12 is the hydrazine of the 1,2-diazene 4. 12 was further characterized by dissolving a small amount in 10 ml of methanol and 0.5g of anhydrous sodium sulfate followed by the addition of *ca.* 0.1g silver oxide. The solution was filtered and purified by gas chromatography yielding a product identical with 4. 12 also slowly converted to 4 in the air over several days.

Pyrolysis of 4 at 130° in a sealed tube for 24 hr yielded a compound with an NMR spectrum consisting of a sinlget at δ 1.6 identical with 2,3-dimethyl-2-butene. (The NMR absorption due to 4 gradually decreased over time as the δ 1.6 peak increased.)

Pyrolysis of 4 in methanol. A 10% solution of 4 in 0.3 ml of methanol was degassed by three freeze-thaw cycles and sealed under vacuum. The sealed tube was immersed in a 150° oil bath for 23 hr. Analytical vapor phase chromatography (SE-30, 110°) revealed only methanol and 2,3-dimethyl-2-butene. The possible ether products methyl 1,1,2-trimethyl-2-propenyl ether and methyl 1,1,2-trimethylpropyl ether, were synthesized according to the method of Kropp.[21] Relative retention times are 4 (1.00), methyl 1,1,2-trimethyl propyl ether (0.66), methyl 1,1,2-trimethyl-2-propenyl ether (0.62), 2,3-dimethyl-2-butene (0.34), and methanol (0.12). The VPC detection limit (Hewlett-Packard 3370A electronic digital integrator) was < 1% of the amount of 2,3-dimethyl-2-butene.

Photoelectron Spectroscopy. The photoelectron spectroscopy was conducted by Frances Houle.[3] For a detailed description of the instrumentation involved in recording the photoelectron spectra of nascent pyrolyses products, see reference 3. The following description of the photoelectron spectroscopy of 4 is from the Ph.D. thesis of Frances Houle.

All spectra were recorded using Helium I radiation and a Tracor-Northern NS570 A multichannel scaler with 4K memory. Pyrolyses were performed at temperatures of 500-800° under conditions of complete decomposition of 4. Resolution was 30 meV for these experiments and the energy scale was calibrated using N_2 and Argon (internal standard) bands. Approximately 5% of the N_2 would have to be excited to appear as signal above spectral noise.

Heating authentic samples of N_2 and 2,3-dimethyl-2-butene produced no evidence of vibrational excitation (indicating thermal equilibrium is not achieved during the short residence time inside the pyrolysis region).

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ABSTRACTS OF PROPOSITIONS

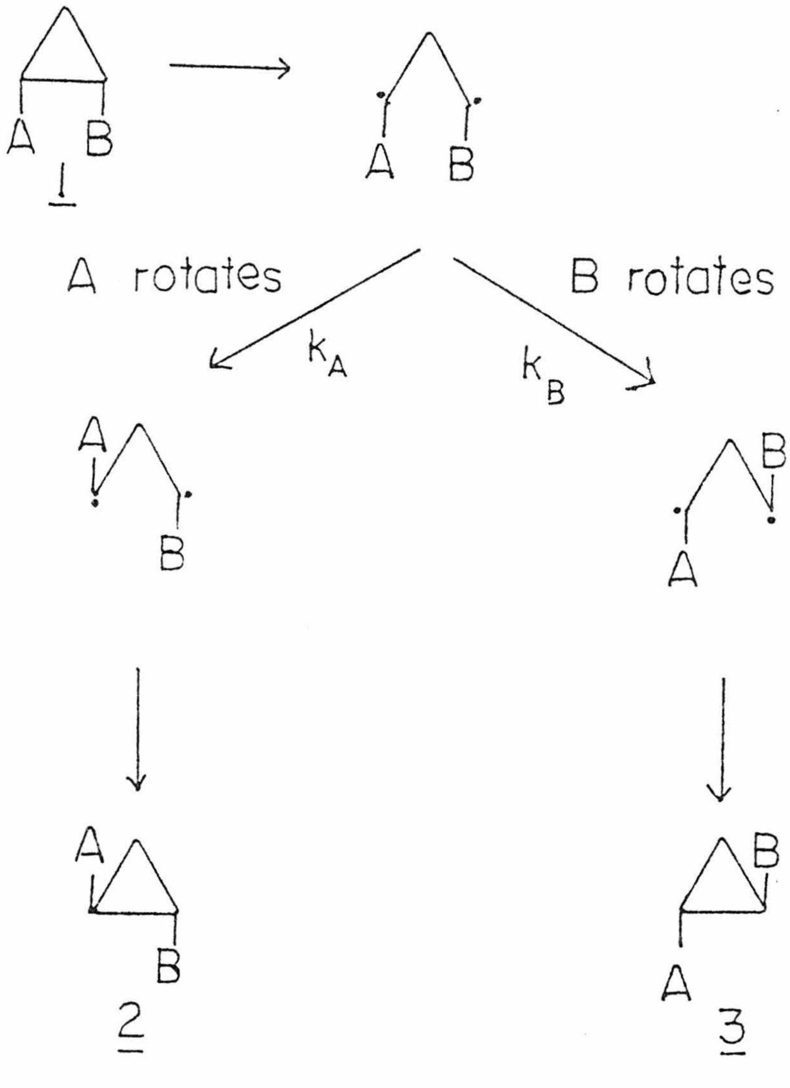
1. A method for measuring relative rotational propensities of differently substituted radical sites in 1,4-biradicals is outlined. A comparison with relative rotational propensities of 1,3-biradicals may provide information on absolute rotational propensities or on differences between 1,3- and 1,4-biradicals.
2. A synthesis of a series of metal nitrosyls is proposed in order to study the effect of ligand donor or acceptor properties on the nitrosyl bonding mode.
3. The pyrolysis of tricyclo[3.1.0.0]hexane at low pressures is suggested in order to study possible chemical activation effects in the unimolecular decomposition.
4. A precursor for generating N-nitrenes by photochemical methods is described.
5. A novel dye release system for instant color photography is proposed.

Proposition 1

RELATIVE ROTIONAL PROPENSITIES IN 1,3- vs. 1,4-BIRADICALS

The factors affecting rotational propensities are not well understood, and efforts to measure absolute rotational rates of variously substituted radicals have not produced consistent results.[1,2] Whether molecular weight, shape, or other physical properties are significant factors in determining rotation rates is notknown.[3,4] A method of study to delineate important factors involves comparing the relative rotation rates of different groups.[3,5,6] In order to isolate the properties which determine why one radical center rotates faster than another, Doering has begun to systematically compare internal rotational propensities in cyclopropanes.[3,4] With reference to Scheme I the question is what is the relative rate of rotation of the radical center with substituent A versus the radical center with substituent B. It can be seen that 2 and 3 are optical isomers and can be distinguished.

Scheme I



Doering has compared several rotational propensities (Table 1).[3,5] He has also found that internal rotation propensities may be additive. That is, if $(R)_A^B = k_B/k_A$ and $(R)_C^B = k_B/k_C$, then $(R)_C^B/(R)_A^B = (R)_C^A$.[5]

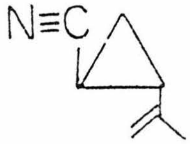
Table 1

Comparison of Rotational Propensities

A[a]	B[a]	$(R)_B^A$
methyl	ethyl	1.2
cyano	isopropenyl	2.2
cyano	phenyl	2.5
isopropenyl	phenyl	1.3
cyano	phenylethynyl	1.8

[a] A and B refer to substituents as shown for 1 in Scheme I.

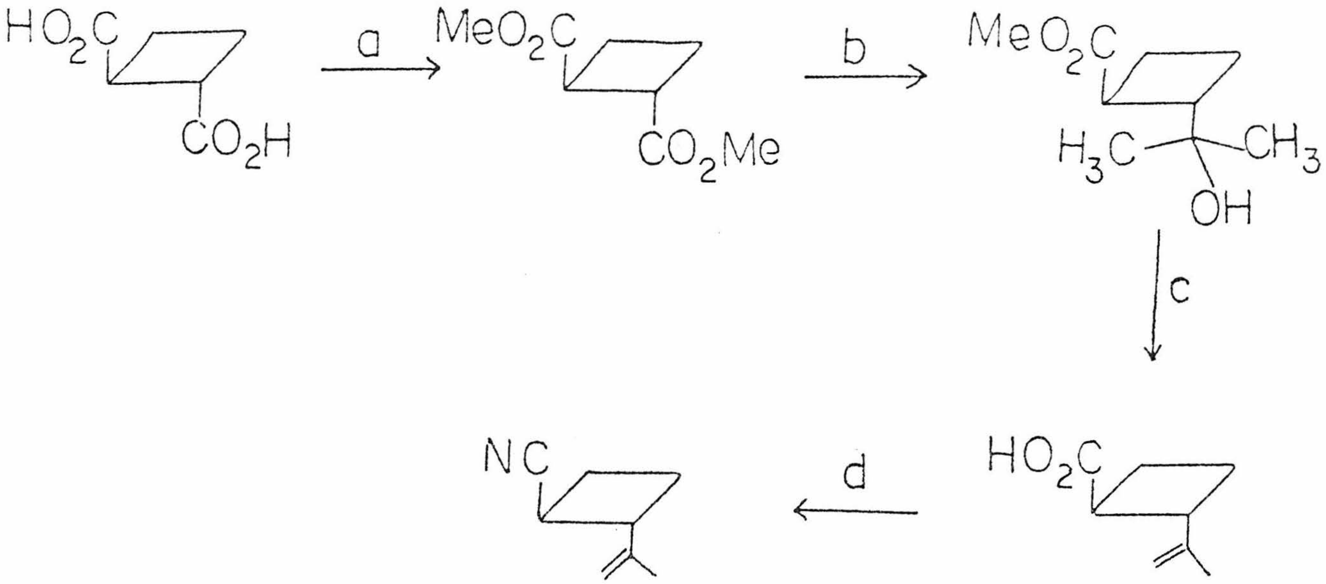
The effect of the substituents at the radical centers upon one another is not known.[3] All of these rates were measured using 1,3-biradicals. A further separation of the radical sites may elucidate this question. Specifically, does $(R)_A^B$ in a 1,3-biradical equal $(R)_A^B$ in a 1,4-biradical? It was found that for 4 $(R)_{i\text{-}Pr}^{CN} = 2.20$.[3] This proposal concerns the synthesis and pyrolysis of 5 in order to measure $(R)_{i\text{-}Pr}^{CN}$ for a 1,4-biradical and test if the relative rotational propensities are conserved.



4

Optically active 5 can be synthesized as described in Scheme II from optically active 1,2-cyclobutane dicarboxylic

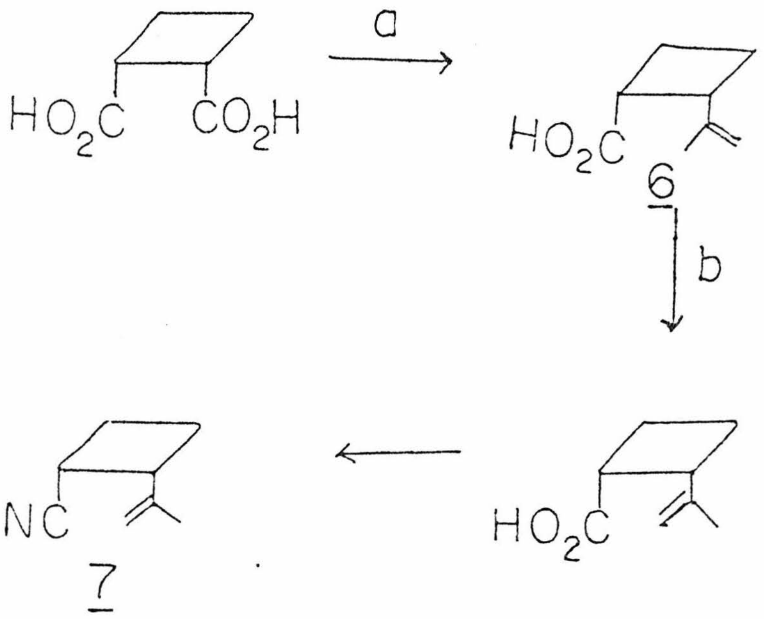
Scheme II



(a) CH_2N_2, (b) CH_3MgBr, 0°, (c) H^+, (d) $OCNSO_2Cl/Et_3N$

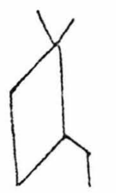
acid.[7] The synthesis of the optically active cis compound is oulined in Scheme III. The important step involves the

Scheme III



(a) See Scheme II, (b) resolve via quinine salt.

resolution 6 (via the quinine salt) and the estimation of optical purity with a chiral shift reagent by NMR. (Tris[3-heptafluorbutylhydroxymethylene)-d camphorato]-europium (III) has been used for this purpose.)[7] The correlation of this compound is possible by comparison with a derivative of α-Pirene, 8.[7] The conversion of

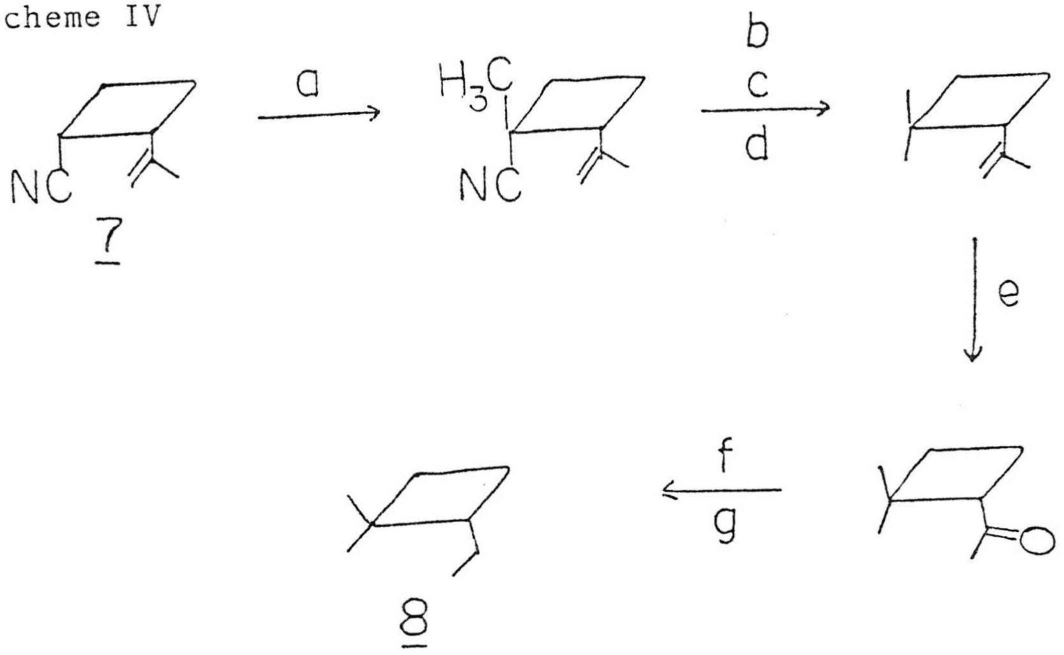


8

S–(+)

optically active 7 to this compound is shown in Scheme IV.

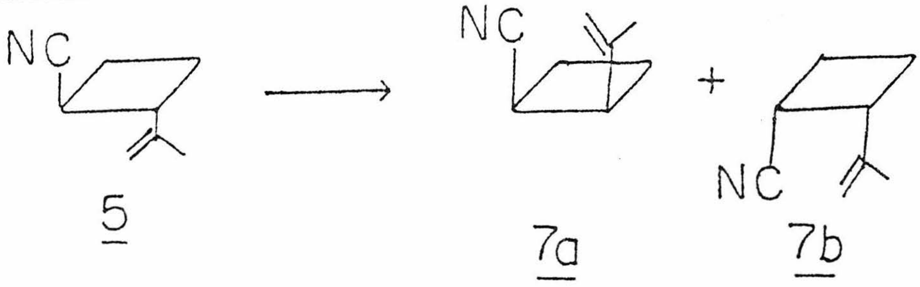
Scheme IV



(a) $LiN(iPr)_2$, (b) H_2SO_4, CH_2N_2, (c) $LiAlH_4$, (d) $MeSO_2Cl$, $LiAlH_4$, (e) O_3, (f) $pCH_3C_6H_4SO_2NHNH_2$, (g) $NaBH_4$.

Compound 5 can be pyrolyzed at low conversions to yield the optical isomers of 7 (Scheme V). The measurement of the optical rotation of isolated 7 directly yields $(R)^{CN}_{i\text{-Propenyl}}$. (For example, if optically pure 5 gives a 90/10 mixture of 7a and 7b (ie, 80% of the rotation of pure 7a), then $(R)^{CN}_{i\text{-Prop}} = 1/9 = 0.11$.)

Scheme V



If the radical sites are independent and the cyclopropane experiments actually measure the intrinsic rotational propensity of each site, the R values from the cyclobutane pyrolyses should be identical. Experiments with other substituents on cyclobutane for further comparisons (Table 1) can be conducted, including tests for the additivity of internal rotational propensities in 1,4-biradicals.

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Proposition 2

NITRIC OXIDE COORDINATION CHEMISTRY

The bonding and bending of transition metal nitrosyls has been a subject of great interest for many years. In order to develop an understanding of the nitrosyl behavior, researchers have gone beyond the simple notions depicted in I and have used molecular orbital theory.

I
linear

I
bent

Hoffman and co-workers used molecular orbital theory in order to develop a simple, usable model which has predictive capabilities for pentacoordinate nitrosyls.[1] Eisenberg and Meyer also conducted a study of this type.[2] The prediction of interest here is that the better the σ- or π-donating ability of the basal ligands (in a square planar with an apical NO geometry), the more likely is the nitrosyl to bend. Hoffman explained this prediction in terms of the metal orbitals. Electron donation raises the energy of the z^2, xz, and yz metal orbitals. Bending relieves the destabilizing interaction between the nitrogen n orbital and the metal z^2 orbital and causes a stabilizing interaction between the π^*_{xz} orbital of NO and the z^2 orbital. This is shown in Figure 1. Conversely, acceptor

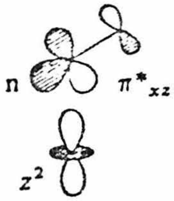


Figure 1. Orientation of the n and π^*_{xz} orbitals of NO with respect to the metal d_{z^2} orbital as the nitrosyl is bent.

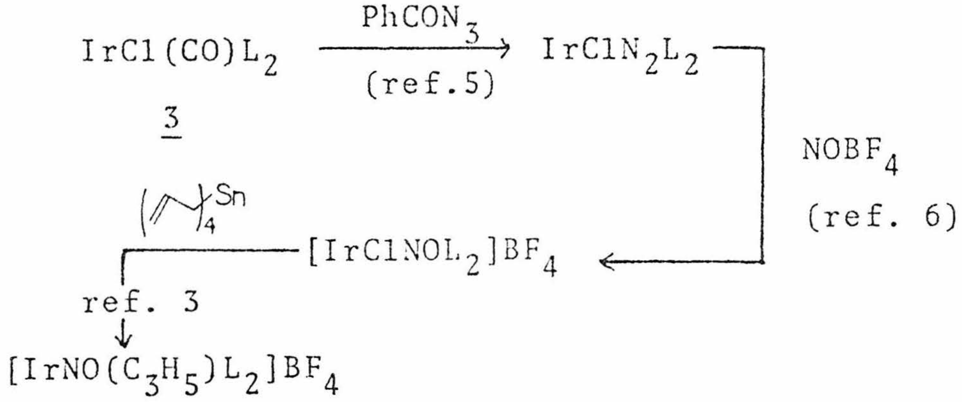
ligands lower the energies of the z^2 and xz orbitals which favor a linear nitrosyl.[1] Eisenberg noted that several options are available to the nitrosyl.[2] Variation of the ligand field to a trigonal bipyramid structure allows maintenance of a strong metal-nitrosyl π interaction (linear) but reduces the effectiveness of σ bonding structure of the entire complex. Maintenance of the square pyramidal structure and the bending of the nitrosyl avoids placing electrons into the strongly antibonding z^2 orbital, but at the cost of metal nitrosyl π bonding. The factors which determine the final geometry include the steric and electronic effects of the ligands and the nature of the central metal. As noted by Hoffman, experimental evidence relevant to the influence of basal ligands on the M-N-O angle is lacking, especially in cases where the donor or acceptor strength is continuously varied.

Recently, Schoonover, Baker, and Eisenberg have synthesized the complex $[Ir(NO)(C_3H_5)(PPH_3)_2]^+$, (2), which has the novel property of a linear $\rightleftarrows$ bent nitrosyl equilibrium.[3] Two nitrosyl stretches were observed in a methylene chloride solution of 2 by infrared spectroscopy. Cooling the solutions caused an increase in the 1763 cm^{-1} band (linear bonding mode) with a simultaneous decrease in the 1631 cm^{-1} band (bent mode). NMR studies showed that the alkyl group was not involved in the transition (only η^3 coordination of the allyl ligand existed in the -50-0° temperature range). The crystal structure of the BF_4 salt of 2 is consistent with a square pyramidal model with the NO in the apical position and the allyl group is bidentate.

This complex provides a system which can be used to conveniently monitor ligand electronic effects on the nitrosyl bonding mode. The lack of data for NO geometry changes when ligand donor or acceptor strength is continuously varied can be alleviated. Since the electronic properties of phosphine ligands (L) are well-documented in the π acidity series,[4] variation of these groups in the complex should cause a shift in the equilibrium which can be observed by IR.

It is proposed that 2 be synthesized in which triphenyl phosphine is replaced with slightly more donating groups such as trimethyl or triethylphosphine and more electron accepting groups such as $P(OMe)_3$ or $P(OPh)_3$. The expectation, according to Hoffman's rules, is that the NO bending mode will be increasingly favored with $P(Me)_3$ while the linear mode would be favored with $P(OMe)_3$. If the equilibrium shifts so much that only one peak is observed, crystal structures may be necessary to identify the NO geometry since IR bands occuring from 1720-1600 cm^{-1} can arise from either structure. Monitoring the geometry of the complex (TBP vs. SP with apical NO) may also be necessary since donating groups may cause a shift to a TBP complex instead of bending the NO.

A synthetic route to the various derivatives of <u>2</u> is shown below.



Compound <u>3</u> (Vasca's compound) can be made with many different L groups as summarized in the work of McAuliffe.[7]

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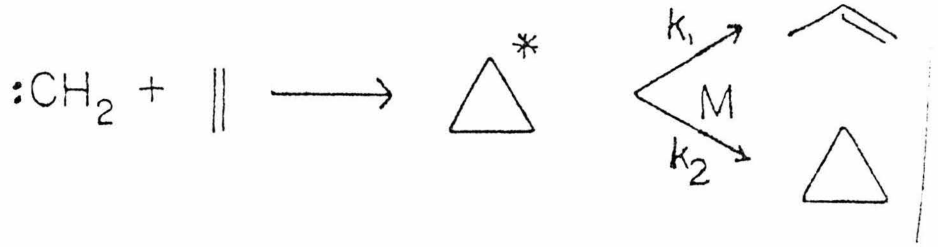
Proposition 3

HOT MOLECULE EFFECTS IN THE PYROLYSIS OF TRICYCLO[3.1.0.0] HEXANE

Chemical activation is the process by which molecules can acquire energy in excess of the average thermal energy by virtue of energy changes in a chemical reaction producing the molecules.[1] These reactions have been important in understanding unimolecular rate theories and reaction mechanisms in which this process is important. Perhaps the most studied systems which show chemical activation are bimolecular association reactions. An example is the reaction between methylene and olefins to produce vibrationally excited cyclopropanes (Scheme I).[1]

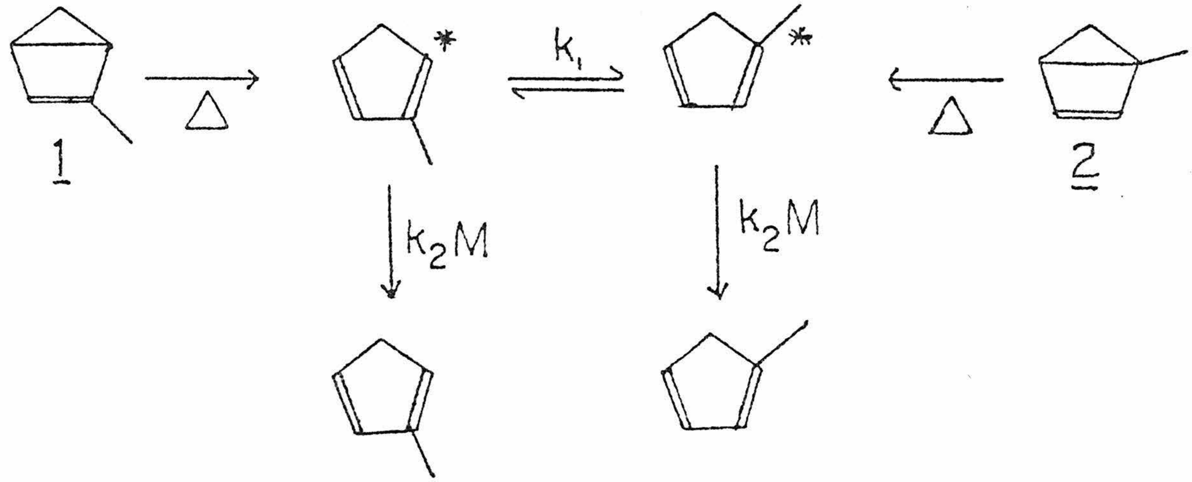
Scheme I



The cyclopropane can be energetically deactived by solvent molecules (M) or decompose to propylene. Also, hydrogen atom reactions with olefins produce activated species.

However, unimolecular rearrangements can also show this behavior.[2-6] The following reaction exemplifies this less established mode of chemical activation (Scheme II).

Scheme II

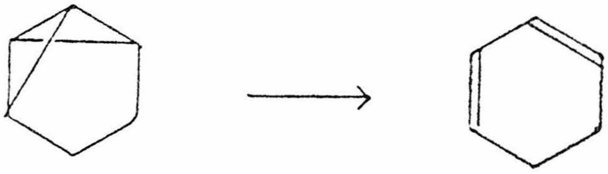


Brauman explained the behavior of 1 by noting that the cyclopentadiene is originally formed with 62 kcal/mol of energy above its ground state. (This is the difference in the heat of formation of compound 1 and of 2-methyl-1,3-cyclopentadiene plus the activation energy for the reaction of 1).[2] Since the energy required for the [1,5] hydrogen shift which transforms 2-methyl-1,3-cyclopentadiene to 1-methyl-1,3-cyclopentadiene is only 27 kcal/mol, the molecule contains 35 kcal/mol of energy in excess of the amount needed to undergo the reaction.

This analysis not only explained the result, it also provided an interesting test of the Rice-Ramsperger-Kassel-Marcus theory of unimolecular reactions. Depending on the excess energy in the reactive species (energized cyclopentadiene in the above example, for instance), the rate of deenergization relative to the rate of rearrangement can be estimated. Frey has carried out calculations on the rearrangement of 1 as a function of bath gas pressure (the higher the pressure, the faster quenching should be).[6] When experimental results were obtained, a comparison showed agreement with the theory provided the strong collision assumption was relaxed.[2] This assumption states that every collision with a bath gas molecule will completely deenergize an activated molecule. Since the cyclopentadiene is initially 35 kcal above the activation energy required for a 1,5 hydrogen shift and most collisions are assumed to remove from 5 to 10 kcal of energy from the excited species (for a fairly efficient bath gas) a stepwise collisional deactivation function was found to more adequately describe the system.[2,7]

Because there are relatively few unimolecular systems in which this type of behavior can be monitored (see references 2 through 6), it is of interest to investigate another system. The rearrangement under consideration for this proposal involves tricyclo[3.1.0.0]hexane 3. Pyrolysis of this compound in the gas phase at 400° in a stream of nitrogen yields exclusively 1,3-cyclohexadiene (Scheme III).[9] The activation energy for this process is 41.7 kcal mol^{-1} (in tetramethylethylene diamine solution).[10]

Scheme III



3 4

The energy surface for this process can be estimated. ΔH_f° (5) = 51.9 kcal mol^{-1} (including 66.5 kcal mol^{-1}) of strain).[11]

5

Using Benson's thermochemical values, two $C-(C)_2(H)_2$ groups must be replaced by two $C-(C)_3(H)$ groups and two $C-(C)_2(H)_2$ groups must be added to find the ΔH°_f of 3. The added strain energy of two five membered rings should also be included (abced and abcfd in Figure 1).[12a]

$$
\begin{aligned}
-2[C-(C)_2(H)_2] &= +10\\
+2[C-(C)_3(H)] &= -4\\
+2[C-(C)_2(H)_2] &= -10\\
\underline{+2[\text{strain in 5 member ring}]} &= \underline{+12.6}\\
\text{so the total} &= 8.6\ \text{kcal mol}^{-1}\ (\text{higher than } 3)
\end{aligned}
$$

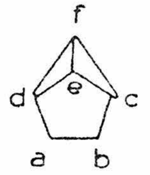


Figure 1. Estimate of the heat of formation of 3. Note that two hydrogens of 5 (at d and c) have been replaced by two CH_2 groups (a and b).

Therefore, ΔH°_f (3) = 8.6 + 51.9 = 60.5 kcal mol^{-1}. The heat of formation of 4 is 26 kcal mol^{-1}.[12b] With this information, the following energy surface can be constructed.

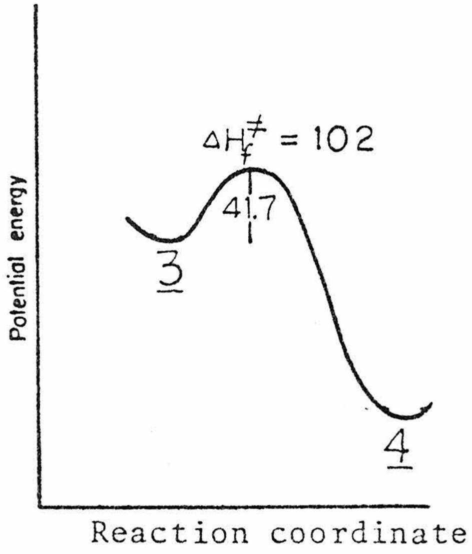
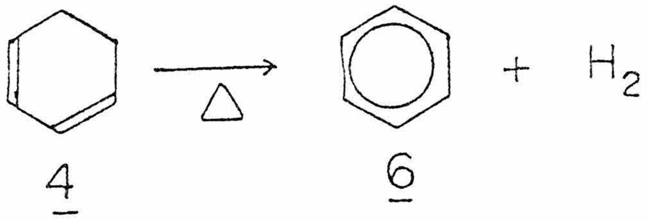


Figure 2. The energy surface for the isomerization of 3 to 4. Values are in kcal mol^{-1}.

The pyrolysis of 4 has also been studied.[13] At 670-800°, at very low pressures, it loses hydrogen to form benzene (Scheme IV). The activation energy for this process

Scheme IV



is 59 kcal mol^{-1}. Since the heat of formation for 6 is 19.8 kcal mol^{-1}, the following energy surface can be constructed.

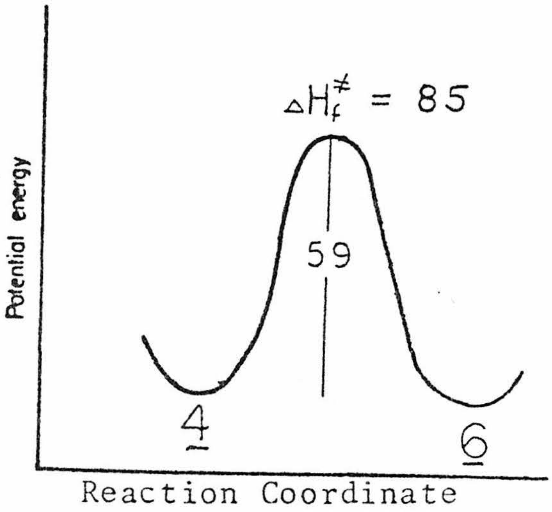


Figure 3. The energy surface for the isomerization of 4 to 6. Energy values are in kcal mol^{-1}.

Evidently, this presents one with an ideal system to investigate chemical activation effects. The conversion of 4 to 6 will not occur (to any appreciable extent) at the temperatures that 3 is converted to 4 since the activation energy for the latter process is 17 kcal mol^{-1} lower. However, due to the strain energy which gives 3 such a high heat of formation, the transition state's heat of formation for the rearrangement of 3 is 102 kcal mol^{-1}, 17 kcal mol^{-1} above the energy needed for the formation of benzene from 1,3-cyclohexadiene.

Therefore, a more complete energy surface, combining Figures 2 and 3 can be constructed.

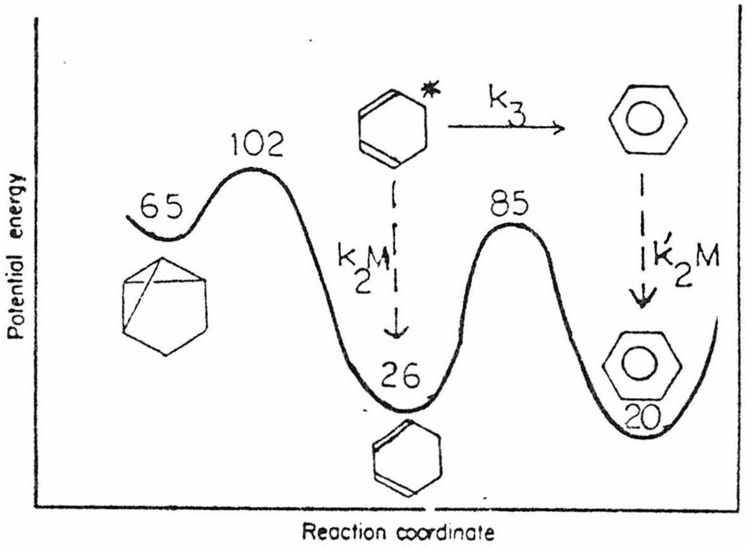


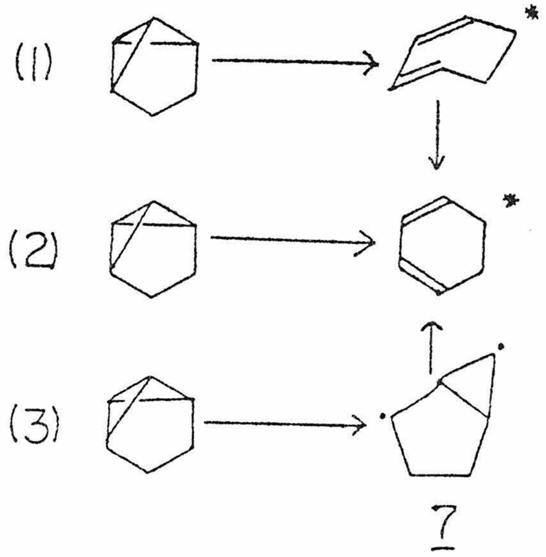
Figure 4. The energy surface for the reaction of 3 to 4 to 6. The values are heats of formation in kcal mol^{-1}.

It is proposed that 3 be synthesized and pyrolized at very low pressures. A system such as the Very Low Pressure Pyrolysis apparatus described by Golden *et al.* would be ideal for this analysis.[14] With this system, the pyrolysis products are analyzed directly by mass spectroscopy. This experiment is also amenable to a more conventional analysis involving pyrolysis in an evacuated tube followed by the collection of the pyrolyzed material and a gas chromatographic analysis of the products

RRKM theory can be used to predict the relative yield of 1,3-cyclohexadiene and benzene as a function of pressure. (As the pressure increases, one expects an increased yield of 1,3-cyclohexadiene over benzene since the activated 1,3-cyclohexadiene is quenched before it can form benzene and hydrogen.) The pyrolysis can be done at increasing pressures of nitrogen, and the results can be compared to the predictions. Usually, the parameters in the theory can be adjusted to give a precise fit, however, the most important adjustment is on the collisional deactivation efficiency. Unlike the bicyclo[2.1.0]pentene system in which the activated molecule is 35 kcal above the activation energy for the [1,5] shift, this system could show closer conformity to the strong collision assumption since 17 kcal mol of excess energy are present and the activation energy for the second reaction is so much higher than the first. The methods for carrying out these calculations for systems such as 3 are outlined in reference 1 and by Frey *et al*. (references 15 and 5).

The mechanism of the rearrangment of 3 has not been completely elucidated. Three pathways have been proposed.[9] These include (1) an allowed ${}_2\sigma_s + {}_2\sigma_a$ isomerization,

(2) a disallowed ${}_{2}\sigma_{s} + {}_{2}\sigma_{s}$ process, or (3) diradical formation.



Recent theoretical studies have favored the diradical pathway since the formation of the highly strained *cis,trans*-1,3-cyclohexadiene formed in (1) appears unlikely and the isomerization of [2.1.0] bicyclobutane may proceed *via* a one bond cleavage, contrary to the previous prediction that a concerted ${}_{2}\sigma_{s} + {}_{2}\sigma_{a}$ process occurred.[10,16] (Thermochemical calculations estimate the heat of formation of the diradical *7* to be *ca.* 101 kcal mol^{-1} which is at the top of the energy surface (see Figure 2).)[17]

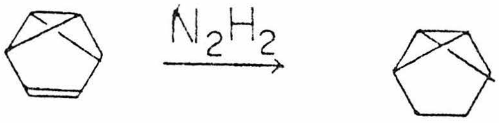
Synthesis of Tricyclo]3.1.0.0]Hexane 3

3 has recently become available in reasonable quantities by combining the syntheses of Katz and Christl.[18,9]

Benzvalene is synthesized as follows.[18]

8

8 is then converted to 3 via reduction with diimide.[9]



8 3

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    (b) Cox, J.P. Tetrahedron 1963, 19, 1175.

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16. Dewar, M.J.S.; Kirschner, S. J. Am. Chem. Soc. 1975, 97, 2931.

17. Derivation of the heat of formation of 7.[12a] $4(C-(C)_2(H)_2) + 2(C-(C)_3(H)) = -24$. Ring correction $= 32$, remove 1 cyclopentyl hydrogen $= 98$, remove one cyclopropyl hydrogen $= 101$, form $H_2 = -104$, cyclopropylcarbinyl stabilization $= -2$. Total $= 101$ kcal mol^{-1}.

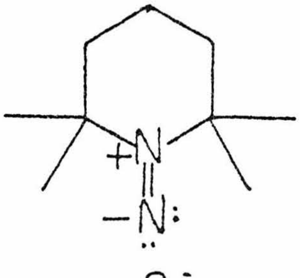
18. Katz, T.J.; Wang, E.J.; Acton, N. J. Am. Chem. Soc. 1971, 93, 3782.

Proposition 4

PHOTOCHEMICAL GENERATION OF N-NITRENES

The assignment of certain reaction mechanisms has been made possible by the direct observation of proposed intermediates.[1,2] Often theoretical predictions precede the experimental determination of the properties of the intermediates. This verification process is important in assessing the value of theoretical methods, not only in determining the quantitative accuracy of the predictions, but also in establishing their qualitative usefulness, that is, proposing whether the intermediate actually exists or not.

In 1977, Goddard and Davis, using generalized valence bond (GVB) and configuration interaction (GVB-CI) wave functions, predicted the existence of 1,1-diazene, H_2N-N (1), in a singlet ground state and estimated the energy of various electronic states.[3] Alkyl derivatives of this compound ($R_2N=N$) had been postulated as intermediates for years, but had never been direct observed.[4] In 1978, Hinsberg and Dervan reported the first observation of a 1,1-dialkyldiazene, 2.[5] They provided evidence that the amino nitrene was a ground state singlet and measured the energy required for the $n\rightarrow\pi^*$ transition which

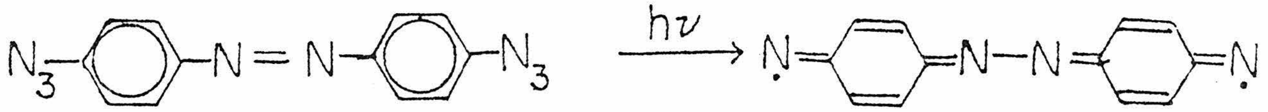


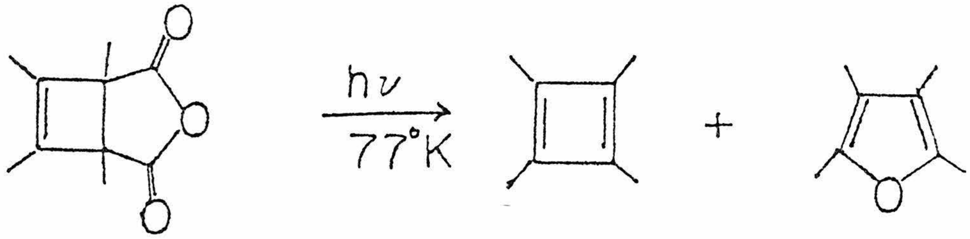
2

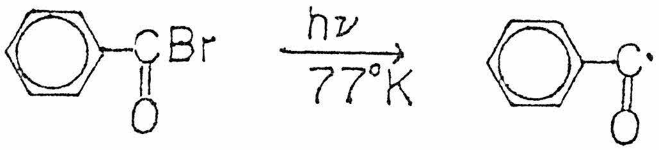
corresponded very closely to the value predicted by Goddard and Davis.[3,4]

Questions that arise concern the effects of different substituents on the nitrogen on the properties of the amino nitrene (ie., the single-triplet energy gap, the geometry, and other electronic state energy spacings). Compound 2 was generated by the tert-butyl hypochlorite oxidation of the corresponding N-amino compound at -78°.[5] This method may have very limited applicability and another method which can generate a variety of N-nitrenes at low temperatures is desirable.

In the past, one of the most successful methods of generating observable transient species has been by low temperature photolysis. A few examples are given below.[2]

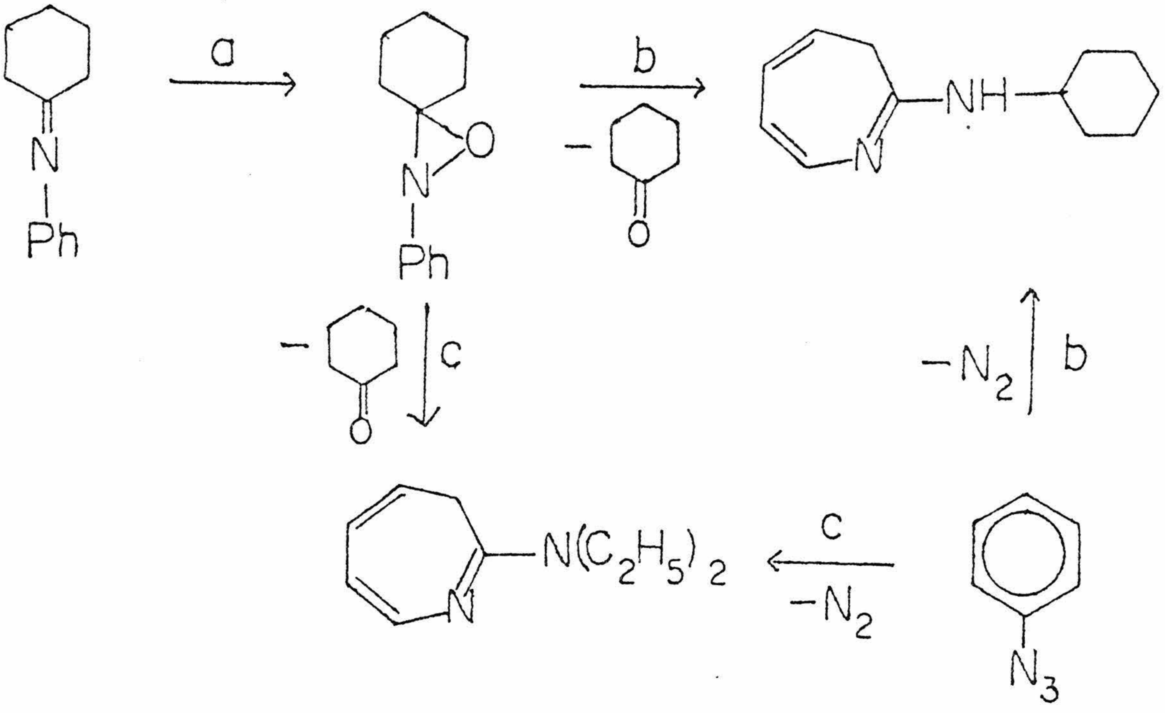






This proposal concerns a method of generating an amino nitrene by photolysis. In 1967, Meyer and Griffin studied the photolysis of oxaziranes and found products consistent with the intermediacy of nitrenes (Scheme I).[6] If N-

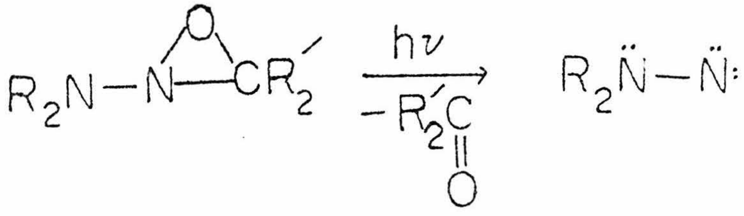
Scheme I



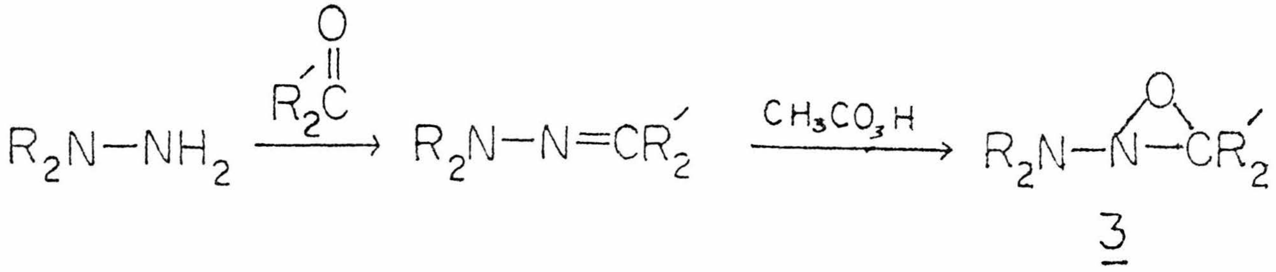
(a) RCO_3H, (b) $C_6H_{11}NH_2/h\nu$, (c) $(C_2H_5)_2NH/h\nu$.

oxaziranes could be synthesized, they could be a source of N-nitrenes by low temperature photolysis (Scheme II). A synthetic route to these compounds is presented in Scheme III. The N-amino compound (which is generally

Scheme II

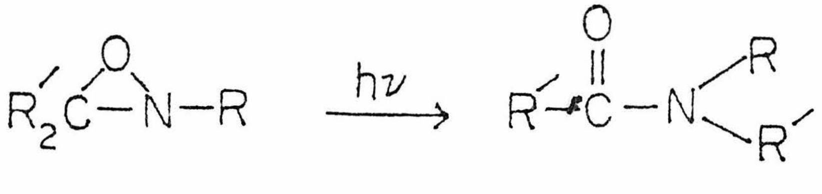


Scheme III



easy to synthesize) reacts with an aldehyde or ketone to give the imine. This can be oxidized with peracetic acid to yield the N-oxazirane (3) which may be isolable.

A fairly extensive body of literature exists on the synthesis, thermolysis, and photolysis of oxaziranes (or oxaziridines).[7] A major pathway of decomposition is shown below.



The effect of the added nitrogen in 3 on the reaction pathway is not known. If this amide producing reaction predominates, the use of N-oxaziridines to generate N-nitrenes will be precluded.

Although the synthesis and photolysis seem reasonably straightforward, there are several variables which must be controlled. It is not known at what wavelength the photolysis will occur, but the wavelength which is chosen must not cause the unimolecular decomposition of the amino nitrene or its reaction with another species (the ketone or aldehyde fragment, solvent, or another amino nitrene molecule). The choice of the carbonyl may allow the use of a desirable wavelength, although it may be advantageous to use acetone, acetaldehyde, or formaldehyde since these carbonyl compounds are fairly volatile and perhaps can be removed from the reaction medium without chromatographic techniques.

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Proposition 5

A NOVEL DYE-RELEASE SYSTEM FOR INSTANT COLOR PHOTOGRAPHY

The development of color photography has been made possible by a complex synthesis of physics, physiology, chemistry, and engineering.[1] The recent development of instant color photography has been made possible primarily because of advances in chemistry.[2,3] In a very oversimplified view of the process, light of a certain wavelength causes the reduction of a silver halide compound which has been sensitized to that wavelength. After the silver ion is reduced, a molecule containing a dye and ballast (to prevent migration) is indirectly oxidized by an electron transfer agent (ETA). The oxidized form of this molecule is susceptible to base attack which releases the dye which migrates to the surface to be viewed.[3] (see Figure 1) The mechanism for a dye release process is shown in Figure 2.

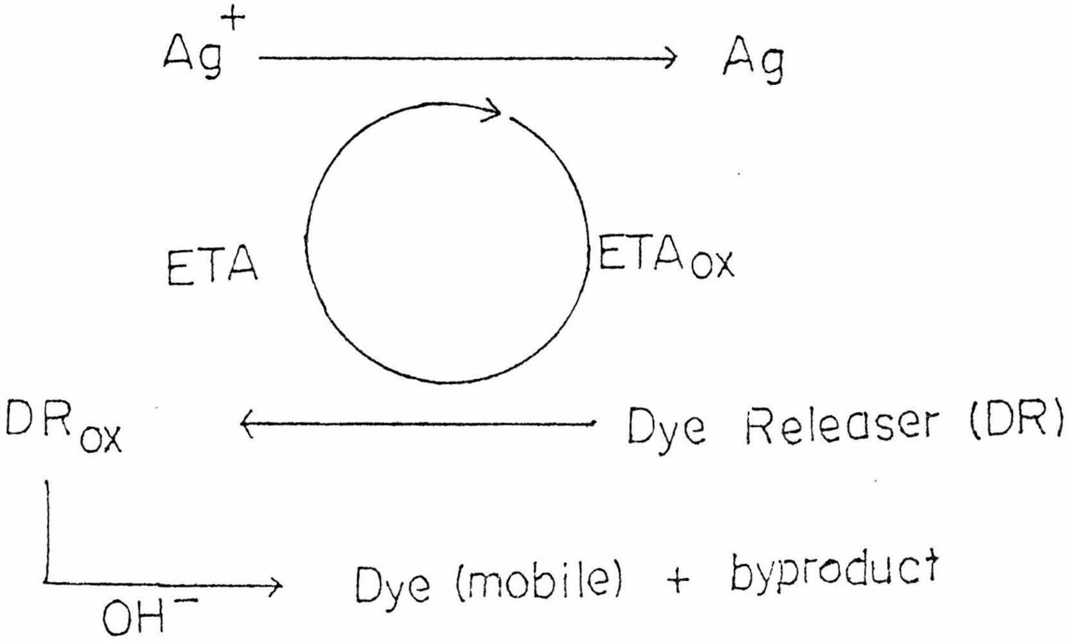


Figure 1. Dye Release Process.

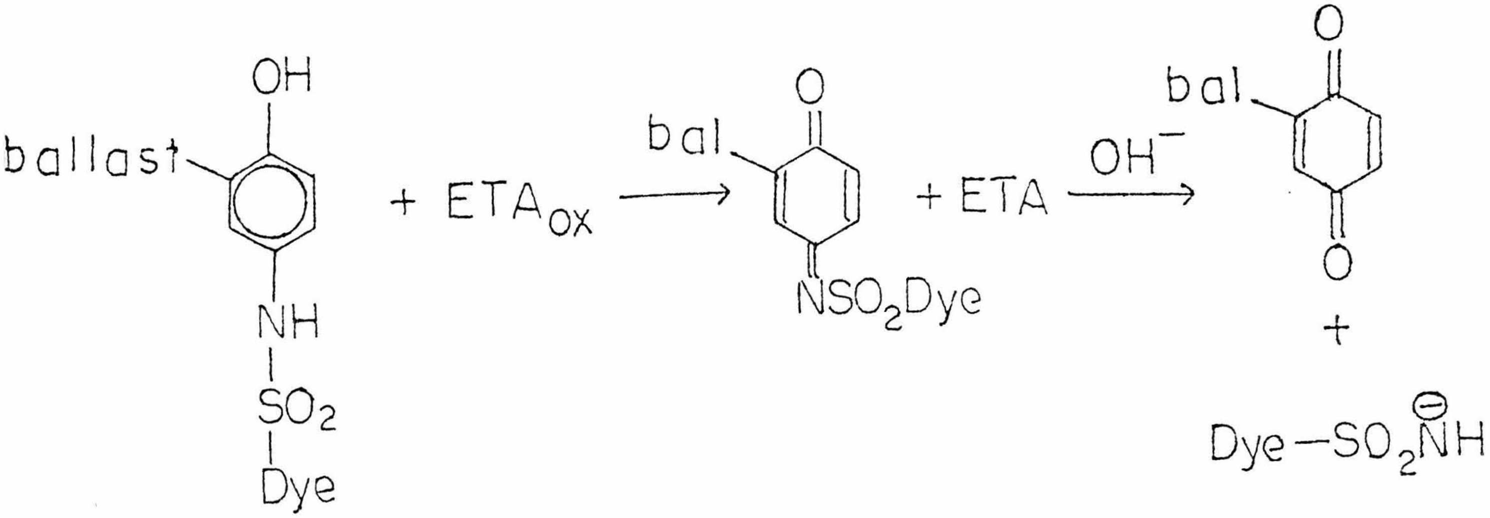
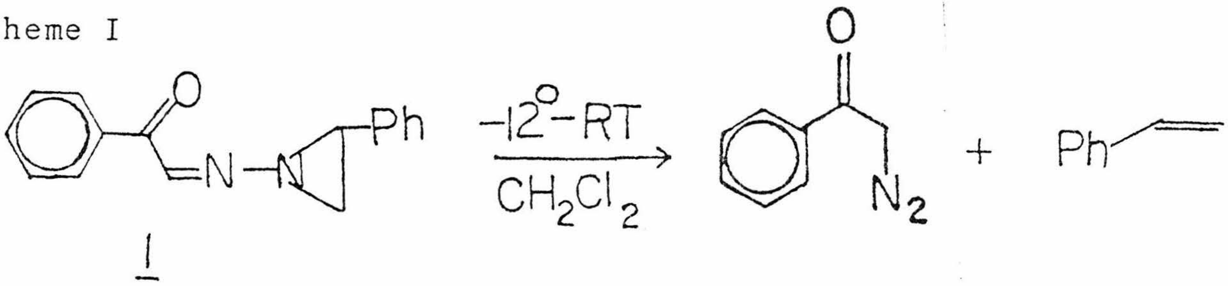


Figure 2. Dye Release Mechanism.

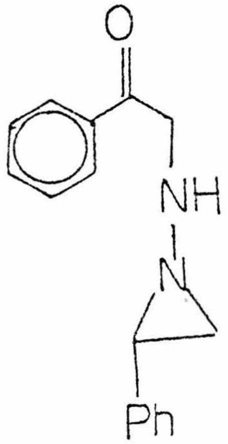
Considerable research is conducted by companies which deal in photography in the search for better color reproduction and picture stability. The search for dyes is wide ranging since normal problems of stability are alleviated due to the dye location in a gel or polymer matrix in a fairly impervious film packet. In instant color photography however, one limitation on the dyes is alkali stability since both Kodak and Polaroid use systems which require fairly strong base.[2]

This proposition is concerned with the development of a dye release process which may alleviate the use of strong base. Eschenmoser has studied the reaction of 1 in CH_2Cl_2.[4] It was found that this compound decomposes spontaneously at room temperature (Scheme I).

Scheme I



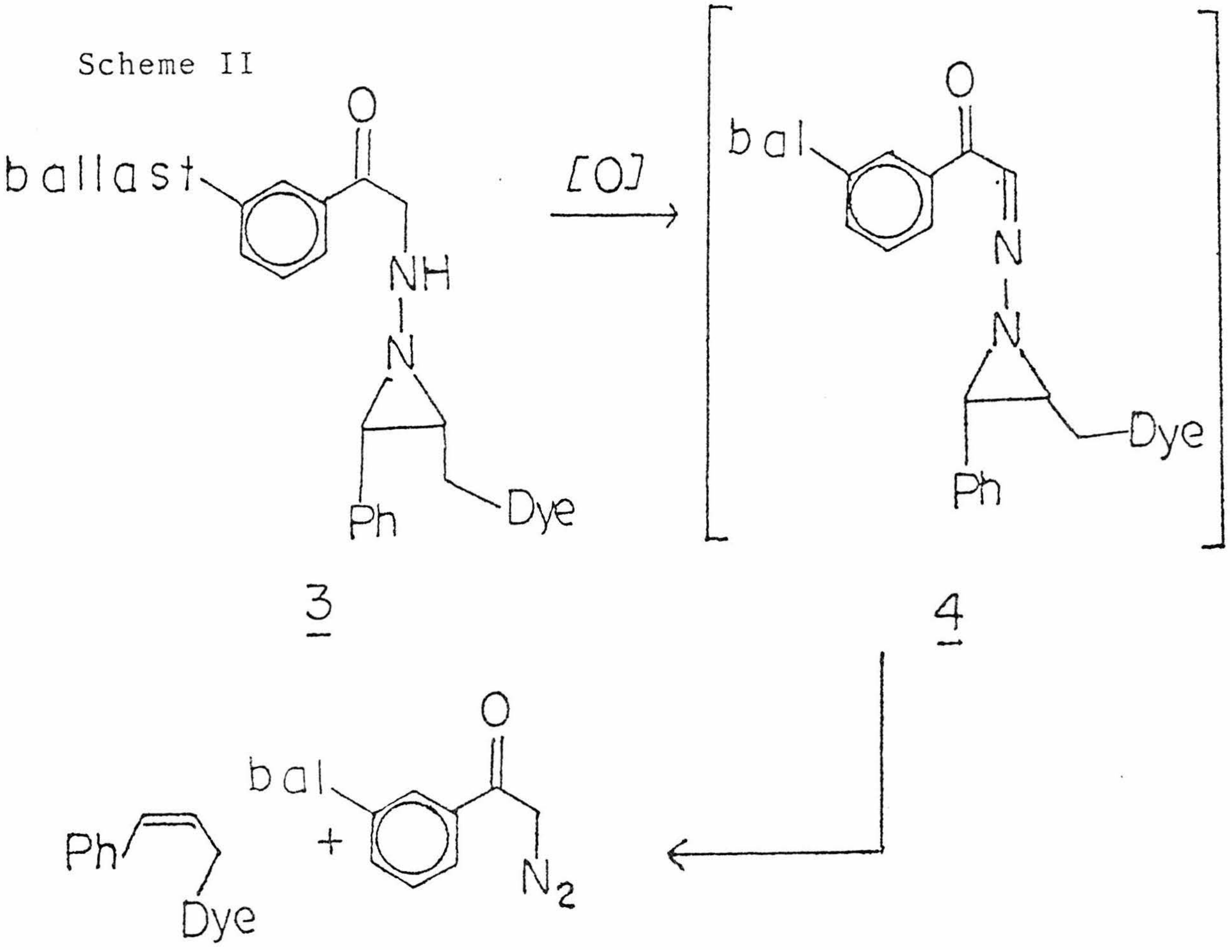
In order to ascertain whether this reaction can serve as the central component of an instant color process, it is necessary to study the stability and oxidizability of 2.



2

The use of 2 in a photographic system is depicted in Scheme II.

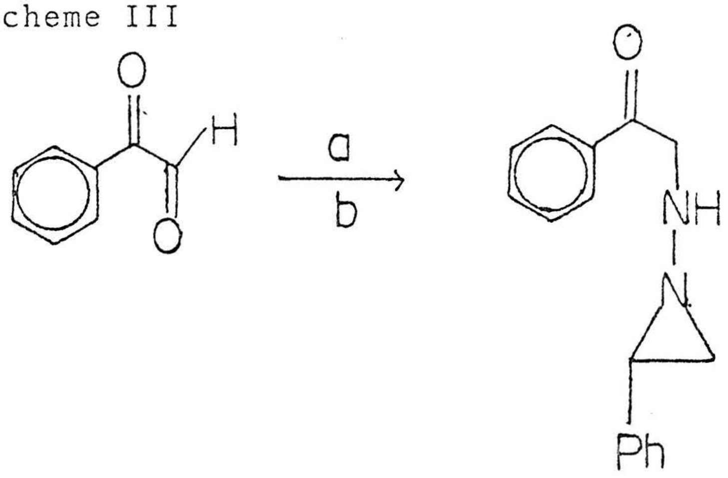
Scheme II



The oxidation of 3, induced by the photoactivation of a silver halide, yields 4 which fragments and releases the dye.

A proposed synthesis of 2 is given in Scheme III. The main obstacle here is the hydrazone reduction in the presence of the ketone. Many selective reducing agents have been developed over the years[5] and a likely candidate is shown in Scheme III.[6] An alternative route involves conversion of the ketone in 1 to a ketal function which protects the group from reduction. Compound 2 must be stable in a gel matrix at temperatures of up to 50°C.

Scheme III



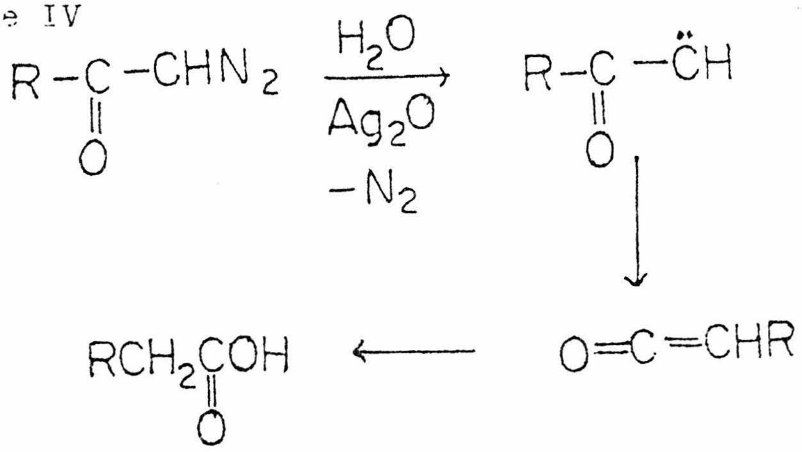
2

(a) $H_2NN(CH_2CHPh)/ < 0°$, (b) Al/Hg, THF/H_2O.

The half-cell potential for the reduction of silver is 0.8V which is sufficient for most organic oxidations. (Oxidation reactions of hydrazines typically have $E_{1/2} \sim$ 0.2V in neutral solutions so the energetics of the reaction are acceptable.)[7] Of course, this does not guarantee that 2 is amenable to oxidation by the systems already developed for photographic systems. Therefore, developing agents (such as 1-phenyl-3-pyrazolidones[3]) must be tested for their ability to oxidize molecules such as 2. (The oxidation of amines to imines by common oxidizing agents such as MnO_4^- has been demonstrated.)[8]

Should 2 be stable and oxidizable to 1, the primary conditions required for its use in instant photography will be met. The actual development of this into a useable system requires extensive "fine tuning" and is certainly beyond the scope of this proposition. For example, in Kodak's process, the dye is released with a minus charge which allows it to be bound to a mordant receiving layer which is a polymer with quaternary ammonium sites.[3] Either a binding function would have to already be included in the dye (since it is attached to a styrene molecule which is not charged) or the receiving layer would have to have an affinity for some other characteristic. Also, the byproduct of the fragmentation is a diazo molecule which may not be stable indefinitely. The Arndt-Eister reaction involves the loss of nitrogen from the diazoketone in the presence of silver oxide and the subsequent rearrangement of the carbene to a ketene which reacts with water to give a carboxylic acid (Scheme IV).[9]

Scheme IV



A possible problem here is the evolution of nitrogen, but it is not expected that enough gas could be released to affect the film packet in any way.[10]

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