THE CHEMISTRY OF 1,4-DEHYDROBENZENES

Thesis by

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..."I must have fallen asleep, for all of a sudden there was the moon, a huge moon framed in the window. Two bars divided it in three segments, of which the middle remained constant, while little by little the right gained what the left lost. For the moon was moving from left to right, or the room was moving from right to left, or both together perhaps, or both were moving from left to right, but the room not so fast as the moon, or from right to left, but the moon not so fast as the room. But can one speak of right and left in such circumstances? That movements of an extreme complexity were taking place seemed certain, and yet what a simple thing it seemed, that vast yellow light sailing slowly behind my bars and which little by little the dense wall devoured, and finally eclipsed..."

-from _Molloy_, by Samuel Beckett

Acknowledgements

My first comments must express the appreciation I feel for the guidance and insight Bob Bergman has provided me. As a scientific mentor he served as a continuous and exciting example of the dynamic application of scientific method. I also gratefully acknowledge the small but tenacious "POC" unit that existed within the research group during my tenure at Caltech and Berkeley. Within this group noble efforts were made to nurse the flame of inquiry into the closets of mechanistic organic chemistry.

I have benefitted enormously, also, from the positive, helpful attitudes which run rampant within the research group. This character has survived, very much intact, being uprooted and transplanted into the cooler Berkeley environment. While these compositions hung suspended in the precarious state of "Works in Progess", the innumerable comments and insights offered by my colleagues were invaluable.

In an extra-academic vein, I want to give my respects to Dr. H. E. Young, DDS, who capped-off my formal education with a dramatic demonstration that, contrary to widely held opinion, graduate school is not nearly as bad as having teeth pulled. Also to David Hume, that wiley fox, who must be the true, if little recognized, ancestor of that branch of inquiry known as mechanistic organic chemistry. Lastly, and most sincerely, I acknowledge the loving support of my parents, siblings, and friends.

Abstract

Upon heating, alkyl substituted cis 1,2-diethynyl olefins undergo cyclization to yield reactive 1,4-dehydrobenzenes; the products isolated may be derived from either unimolecular or bimolecular reactions of the intermediate. Z-4,5-Diethynyl-4-octene (**19**) undergoes rearrangement to yield 2,3-di-n-propyl-1,4-dehydrobenzene (**33**). Solution pyrolysis of **19** in inert aromatic solvents produces three unimolecular products, (Z-dodeca-4,8-diyn-6-ene (**23**), benzocyclooctene (**25**) and o-allyl-n-propylbenzene (**26**)) in high yield. When 1,4-cyclohexadiene is added to the pyrolysis solution as a trapping agent, high yields of the reduced product o-di-n-propylbenzene (**28**) are obtained. The kinetics of solution pyrolysis of **19** in the presence and absence of trapping agent establish that 2,3-di-n-propyl-1,4-dehydrobenzene is a discrete intermediate on the pathway leading to products. When the reaction was run in the heated probe of an NMR spectrometer, CIDNP was observed in **26**. This observation, along with kinetic and chemical trapping evidence, indicates the presence of two additional intermediates, formed from **33** by sequential intramolecular [1,5] hydrogen transfer, on the pathway to products. The observation of CIDNP, coupled with the reactivity exhibited by **33** and the other two intermediates, implicates a biradical description of these molecules.

Two approaches have been used to determine the spin state(s) of 1,4-dehydrobenzenes produced in the solution reaction of diethynyl olefins. The first method relies on the "spin

correlation effect" which postulates a relationship between the spin state of a caged radical pair and the ratio of cage and escape reactions (C/E) which may occur in the pair. When the 2,3-di-n-propyl-1,4-dehydrobenzene biradical abstracts hydrogen from 1,4-cyclohexadiene, a radical pair is generated. If a mixture of 1,4-cyclohexadiene-d_0 and -d_4 is employed it is possible, by performing a VPC-MS analysis, to determine the ratio C/E leading from the radical pair to the reduced product, **28**. Applying this method to the reaction of **19**, C/E was found to be 0.6, independent of the concentration of 1,4-cyclohexadiene (between 0.1 and 10 M) in the chlorobenzene reaction solution. This result suggests the presence of the singlet state of **33** in the reaction of **19**. Independent support for this analysis came from the reaction of 3,4-dimethyl-1,5-diyn-3-ene (**38**) in hexachloroacetone solvent in an NMR probe. The major product, 1,4-dichloro-2,3-dimethylbenzene (**39**), obtained by chlorine abstraction from the solvent, showed polarization (emission) in the aromatic protons. The interpretation of this result is straightforward and indicates solvent trapping of the singlet state of the intermediate 2,3-dimethyl-1,4-dehydrobenzene. Both of these experiments indicate that only the singlet state of 1,4-dehydrobenzenes is generated upon thermal reaction of diethynyl olefins. The failure to observe evidence for the triplet state of the 1,4-dehydrobenzenes under the reaction conditions requires that, if the triplet is the ground electronic state, the rate of intersystem crossing from the singlet must be $<10^9$ sec^{-1}.

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THE CHEMISTRY OF 1,4-DEHYDROBENZENES

Chapter I

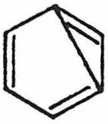
INTRODUCTION

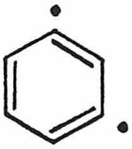
General

The highly reactive group of isomeric dehydrobenzenes, or benzynes, have provided challenging synthetic, mechanistic and theoretical targets for a number of years.[1] Of particular interest in these molecules is the extent of interaction between the dehydro-centers. The o-benzyne isomer (**1**) has been well characterized experimentally; it has been studied spectroscopically[2] in a matrix at 8° K and its reactivity toward a variety of substrates examined.[1a,b] These studies indicate that substantial pi-bonding exists between the dehydro-centers.

1

The 1,3-[3] and 1,4-dehydrobenzenes[4-12] have been much less yielding to experimental investigation. For both 1,3- and 1,4-dehydrobenzene bicyclic and biradical structures (**2a,b; 3a,b**) must be considered. Offsetting the energetic gain of forming a bond between the dehydro-centers is the substantial strain energy associated with the bicyclic structures. In addition, the bicyclic 1,4-dehydrobenzene (butalene) may be further destabilized due to antiaromatic cyclobutadiene resonance. The 1,3- and 1,4-dehydrobenzenes may be molecules, then, in which the gain in energy due to bonding of the unpaired electrons is more than offset by the increase in strain energy. Thus they may belong to a small, unusual class of organic molecules containing a negative bond dissociation energy.[13] An additional consideration regarding the biradical structures is whether the lowest energy open-shell electronic state is a singlet or a triplet. The relative energies of these spin states will depend on the extent of interaction between the dehydro-centers.[14]


2a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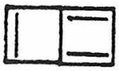

3a

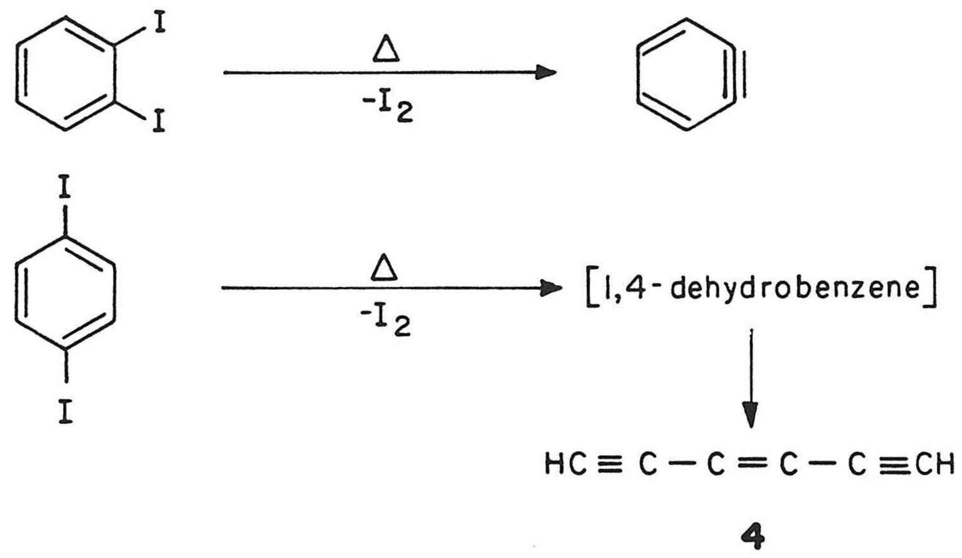

3b

The possibility that **2** and **3** may possess several energetically similar structures has made them challenging subjects for study. 1,4-Dehydrobenzene is the subject of the investigations reported in this dissertation.

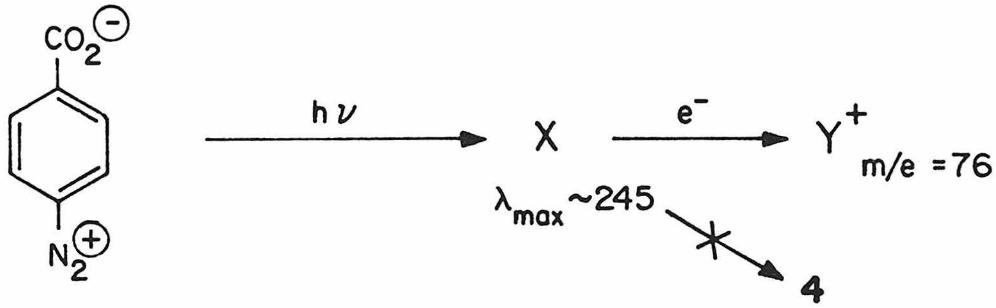
Literature Survey

The first reported attempt to generate 1,4-dehydrobenzene was made by Fischer and Lossing[4] in 1963, who examined the pyrolysis of 1,4-diiodobenzene (they had previously produced o-benzyne by the similar pyrolysis of 1,2-diiodobenzene; Scheme I). Mass spectroscopic analysis of the pyrolysate showed the formation of a compound with a highest m/e peak at 76 and an

Scheme I



Scheme II

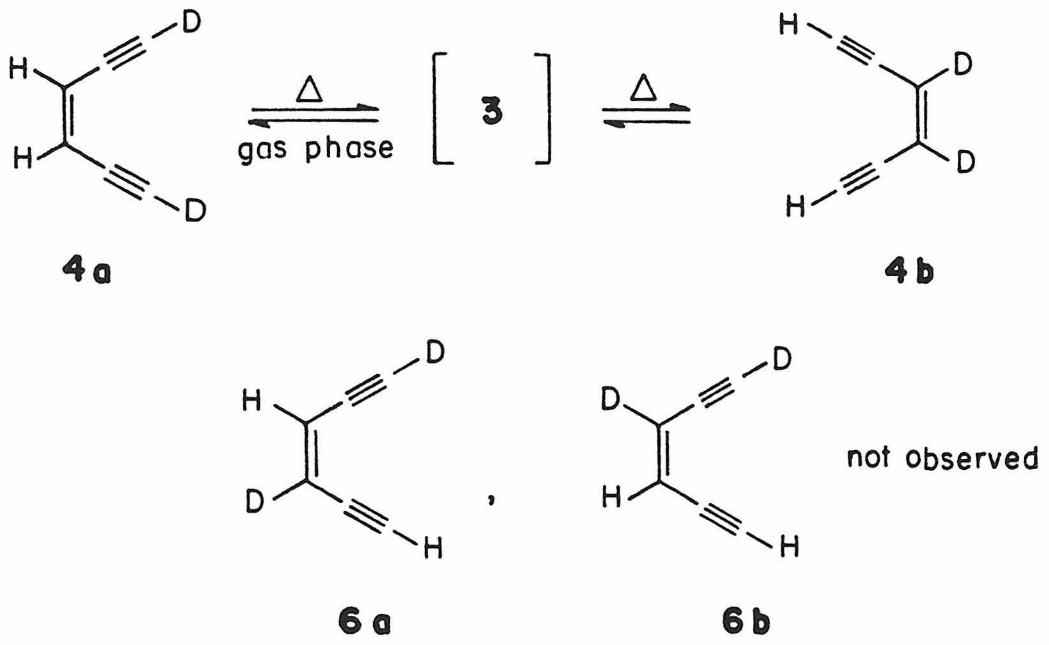


ionization potential of 9.46 eV. From these data they assigned the product of the pyrolysis to diethynyl olefin **4**.

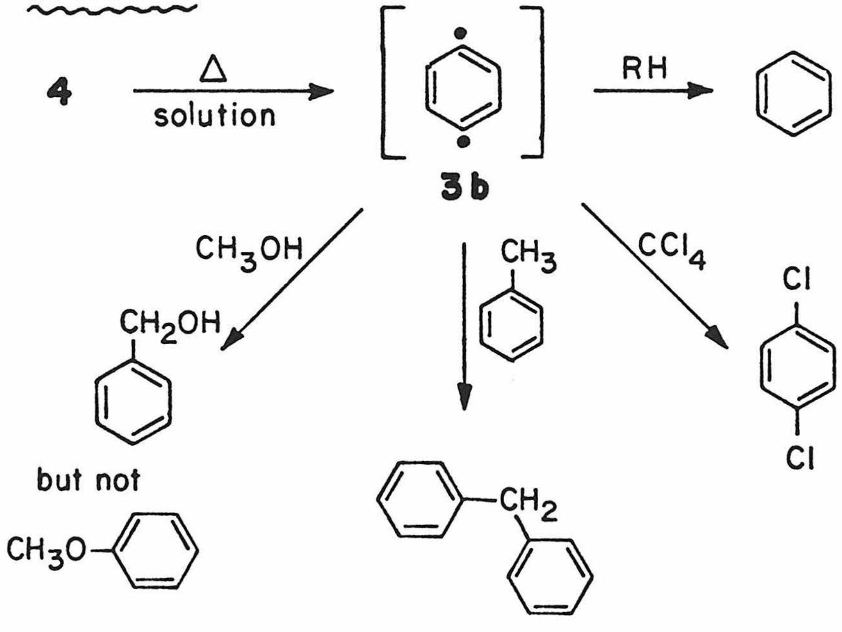
Berry and coworkers[5] attempted to generate 1,4-dehydrobenzene by the photolysis of compound **5** (Scheme II). Monitoring the reaction by flash-absorption optical spectroscopy and time-resolved mass spectroscopy, they observed a signal at m/e 76. From time-of-flight experiments they estimated the lifetime of the species, **X**, giving rise to the m/e 76 peak to be greater than 2 minutes under their experimental conditions (high vacuum, temperature unspecified). No evidence was obtained for the formation of **4** in this reaction. From these experiments it is not possible to distinguish the case where **X** is 1,4-dehydrobenzene from that where **X** is a meta-stable compound which falls apart under ionizing current to a compound (not necessarily 1,4-dehydrobenzene) having m/e 76.

Further work in this area was not forthcoming until Jones and Bergman[6] performed the experiments summarized in Scheme II. The equilibration of **4a** and **4b** took place in the gas phase at 200° C and only products containing two deuteria per molecule were observed. This suggested that the reaction was unimolecular. The observation that neither **6a** nor **6b** were produced in the reaction indicated the presence of a transition state or intermediate (a 1,4-dehydrobenzene) containing a new C_2 axis of symmetry. Pyrolysis of **4** in various solvents (Scheme IV) provided evidence that 1,4-dehydrobenzene was indeed an intermediate of finite lifetime. Furthermore, the abstraction of hydrogen from a hydrocarbon solvent (RH) and chlorine from CCl_4

Scheme III



Scheme IV

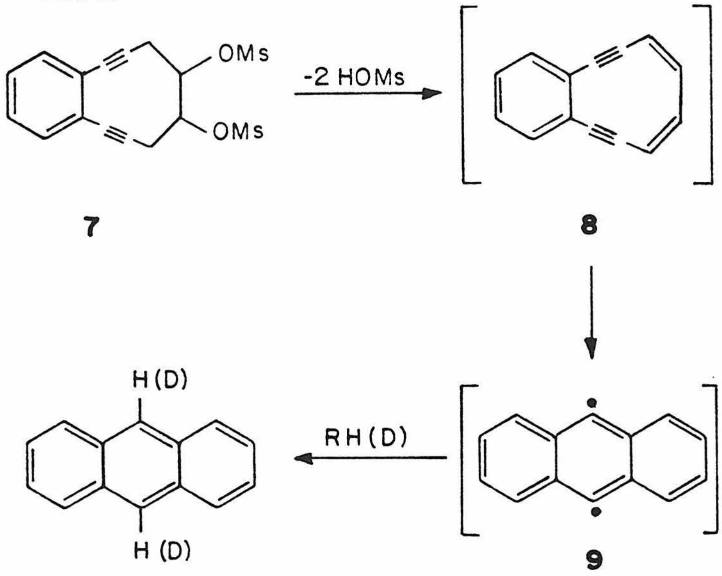


strongly suggested a biradical structure (**3b**) for at least the _reactive_ form of the intermediate. The trapping observed with methanol argued against a zwitterionic description of 1,4-dehydrobenzene, which would have been expected to produce anisole.

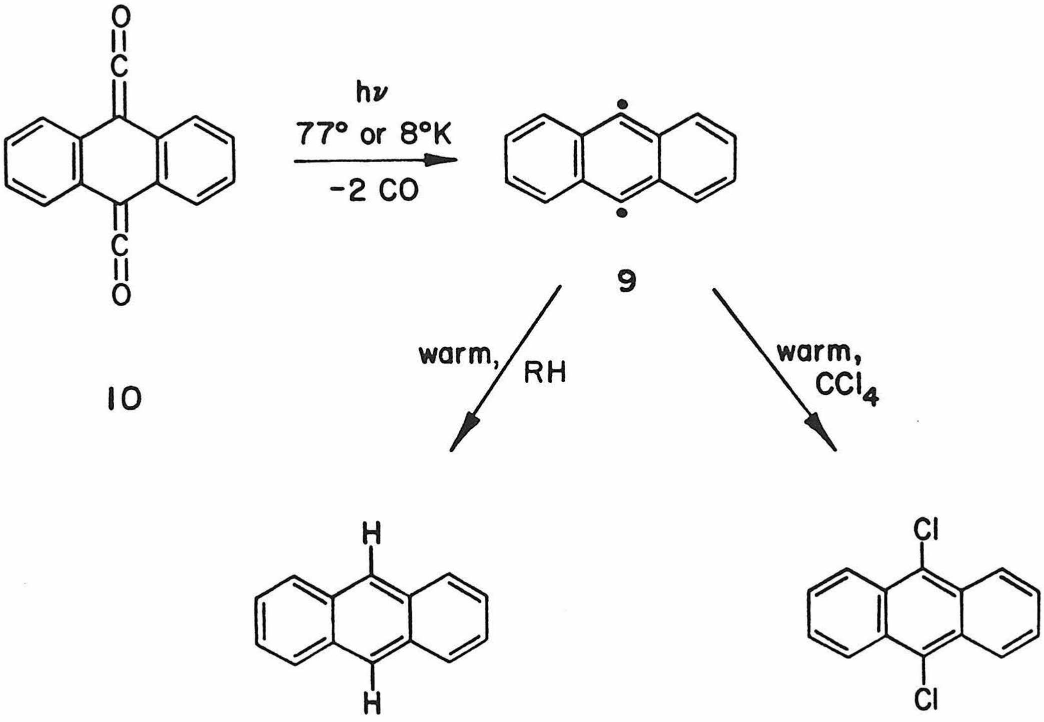
Experiments reported by Chapman and Masamune on related 1,4-dehydroaromatics also provided support for biradical structures. Masamune, _et al_.[7], performed the elimination of two equivalents of methanesulfonic acid from dimesylate **7** to give **8** (Scheme IV) which contains the elements of a diethynyl olefin within a ten membered ring. The strain in compound **8**, presumably, is responsible for the mild temperature (_ca_. 25° C) at which further rearrangement occurs. In fact, **8** was never successfully isolated. Abstraction of hydrogen from the solvent is consistent with the formation of 9,10-dehydroanthracene **9** in this reaction, in analogy with the results of Jones and Bergman.

Chapman and coworkers[8] studied the photolysis of **10** in both a hydrocarbon glass and an argon matrix (Scheme V). When the photolysis was carried out in a hydrocarbon glass, anthracene was obtained upon warming the photolysate to room temperature. Doping the hydrocarbon glass with CCl_4 produced 9,10-dichloroanthracene upon warming. These results suggest the formation of a 9,10-dehydroaromatic intermediate which reacted as a biradical even at subambient temperatures. The low temperature photolysis of **10** was also monitored by ESR; failure to observe an ESR signal in these experiments provides negative evidence in

Scheme IV



Scheme V



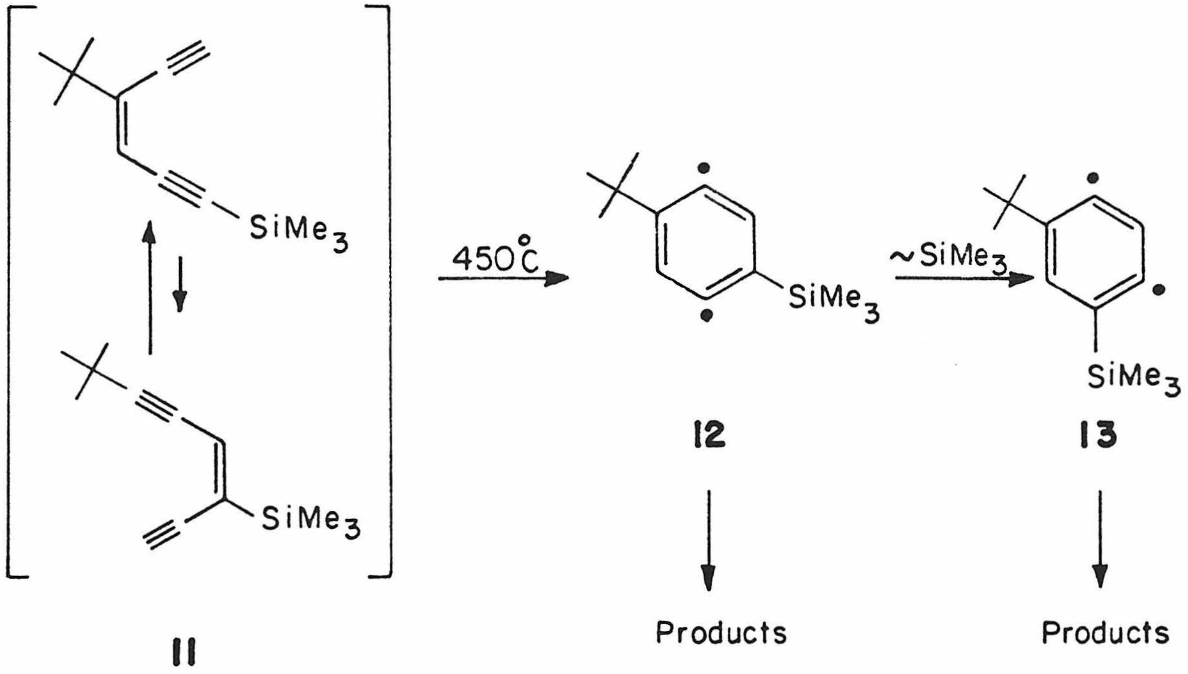
favor of a singlet ground state in **9**.

A provocative result was recently reported by Gilbert Johnson from this laboratory.[9] The products obtained from thermolysis of diethynyl olefins **11** indicated that at elevated temperatures a novel trimethylsilyl migration in the substituted 1,4-dehydrobenzene **12** occurred to produce 1,3-dehydrobenzene isomer **13** (Scheme VII). This is the only reported example of interconversion of dehydrobenzene isomers.[10]

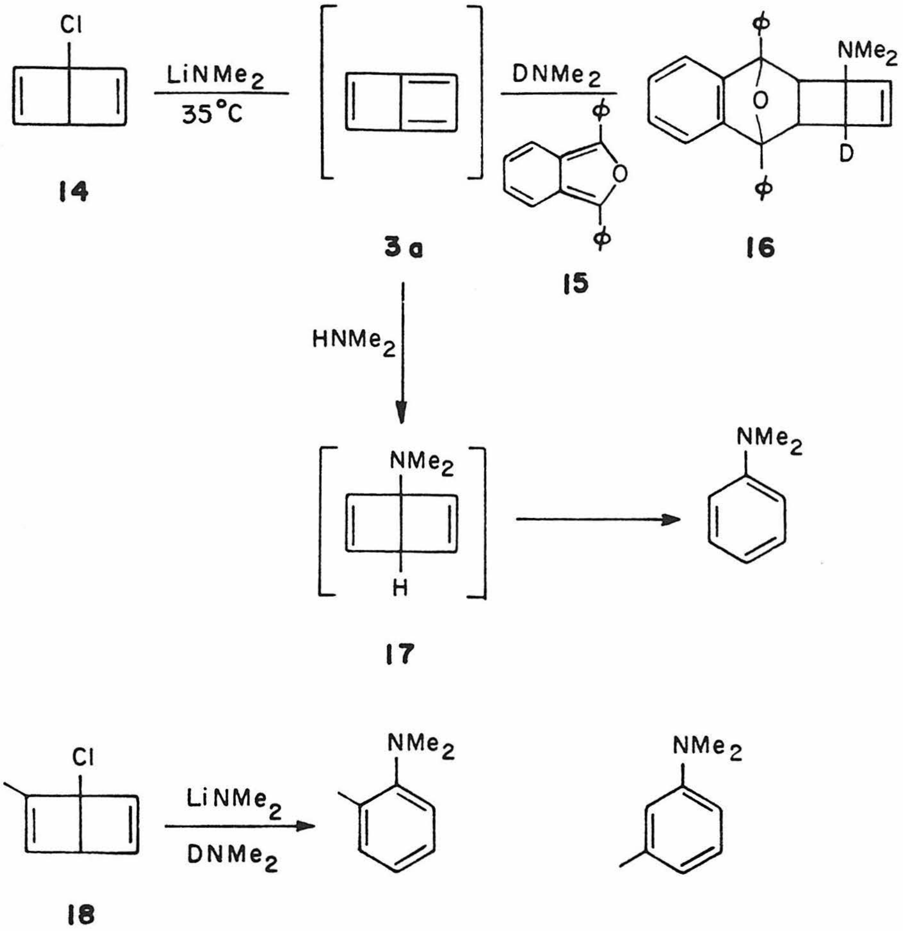
In contrast to the studies cited above, in which the 1,4-dehydroaromatics clearly display biradical reactivity, Breslow, et al.[11], have reported evidence which suggests that they have generated and trapped the bicyclic isomer, butalene (**3a**). Their approach was to employ a base-induced elimination of HCl from Dewar benzene **14** (Scheme VIII). When the reaction was performed in the presence of 1,3-diphenylisobenzofuran, **15**, Diels-Alder trapping of (presumably) 1-deuterio-4-dimethylaminebicyclo-[2.2.0]-2,5-hexadiene (**17**) produced a modest yield of **16**. In the absence of trapping agent dimethylaniline was obtained. These results, especially the formation of **16** in which the 1,4-bond remains intact, are consistent with a mechanism in which butalene is an intermediate.

In a subsequent study by Breslow and coworkers,[12] 1-chloro-2-methylbicyclo-[2.2.0]-2,5-hexadiene **18** was treated with strong base in a deuterated solvent ($DNEt_2$). Both the position of methyl substitution and the amount of deuterium incorporation (d_0 to d_3) in the N,N-diethyltoluidine products indicated that the reaction is considerably more complicated than it was originally

Scheme VII


SiMe3
SiMe3
450°C
SiMe3
~SiMe3
SiMe3
11
12
13
Products
Products

Scheme VIII

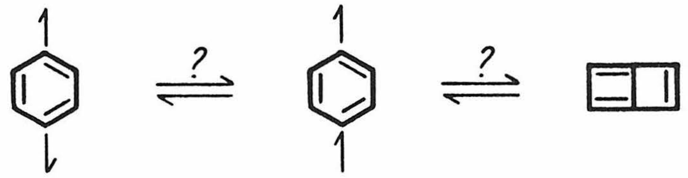


relative yield:	80 %	20%
	% d_n	% d_n
d_0	53	21
d_1	31	42
d_2	14	27
d_3	2	9

thought to be. It was necessary to conclude from this study that the butalene intermediate may not be on the major pathway leading to the N,N-dimethylaniline products, although it was still presumed to be the precursor of **16.** The complexities encountered in this work arose in large part from the relatively harsh conditions (strong base) employed to induce the elimination reaction.

Coincident with the efforts of experimentalists to generate and characterize the reactivity of 1,4-dehydrobenzene, a number of theoretical treatments have been carried out (Table 1).[15-19] Wilhite and Whitten[16] reported a detailed *ab initio* study in which three calculations were performed: a full SCF-MO treatment of both the singlet and triplet electronic states, a limited configuration interaction (CI) calculation, and a many-determinant CI treatment. The simplest calculation predicted that the energy of the triplet biradical lies well below that of the singlet. Inclusion of CI in the calculations, however, led to a much smaller predicted difference in the singlet and triplet biradical energies. The smallest energy difference was predicted in the full CI calculation which placed the triplet state 3.5 kcal/mole below the singlet. In these calculations, the geometry of 1,4-dehydrobenzene was somewhat arbitrarily taken to be that of benzene. Whilhite and Whitten were careful to point out that, given the small singlet-triplet energy difference found, a calculation performed at the equilibrium geometry might lead to an inverted ordering of the electronic states. Because the

Table 1 Calculated Energies of 1,4-Dehydrobenzene Structures



	Relative Energy of Structures (kcal/mol)		
	Triplet	Singlet	Singlet
Wilhite, Whitten (1971)(16) SCF–MO–CI	0	+3.45	–
Dewar *et al.* (1974)(17) MINDO|3; lim. CI	+5	0($\Delta H_f = +117$)	+36
Washburn *et al.* (1979)(3a) Ab initio, 4–31G (no CI)	0	(+82)	+94
Mueller (1973)(19) Modified MINDO|2 (no CI)	0	(+24)	+18
Noell and Newton (1979)(18) Ab initio GVB; 4–31G	+1.4	0	–

geometry was fixed in their treatment, no prediction was made concerning the position of butalene (which would be expected to have a much shorter 1,4 distance than benzene) on the energy surface.

Dewar and Li[17] reported a MINDO/3 study in which geometry optimization was carried out for the singlet and triplet electronic states. The singlet biradical was predicted to be 6.2 kcal/mole more stable than the triplet. An investigation of the singlet surface led to the prediction that butalene lies in a relative energy minimum, 35.9 kcal/mole above the singlet biradical. The transannular bond in butalene was predicted to be 1.667 A long.

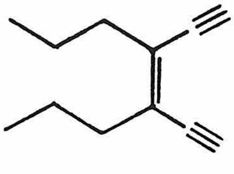
A generalized valence bond (GVB) calculation of the 1,4-dehydrobenzene energy surface was recently reported by Noell and Newton.[18] These authors performed limited geometry optimization for the singlet and triplet states. They concluded that the lowest energy structure of 1,4-dehydrobenzene is the singlet biradical and that the bicyclic butalene structure lies in a local energy minimum very roughly estimated to be 77 kcal/mole higher. The triplet biradical was calculated to have an energy slightly above that of the singlet (1.4 kcal/mole), though the difference calculated for the two biradicals appears to be less than the uncertainty of the calculations.

To summarize the experimental and theoretical work on 1,4-dehydroaromatics, the most convincing cases for its generation suggest that a biradical description is appropriate. The two important geometry-optimized theoretical studies of the 1,4-

dehydrobenzene energy surface are in agreement in predicting that the bicyclic isomer lies substantially higher in energy than the biradicals. The possibility exists, however, that the bicyclic structure is lowest in energy but undergoes either facile 1,4-bond cleavage or suffers 1,4-cleavage in concert with atom abstraction reactions. Convincing experimental evidence for the existence of butalene as a meta-stable species must await its generation and characterization under extremely benign conditions, such as in an argon matrix.

Goals

One of the goals of my research has been to obtain kinetic evidence for the existence of a discrete 1,4-dehydrobenzene intermediate in the thermal reaction of diethynyl olefins. We were also interested in further characterizing the reactivity of the 1,4-dehydrobenzene intermediate produced in these reactions. Chapter II of this dissertation describes a mechanistic investigation of the thermal reaction of Z-4,5-diethynyl-4-octene (**19**) which provides compelling evidence for the occurrence of a true 1,4-dehydrobenzene intermediate on the pathway leading to products. It was also hoped that evidence for the spin state of the 1,4-dehydrobenzene intermediate(s) present in these pyrolyses could be obtained; Chapter III details the results of our efforts in this area.



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Chapter II

CHEMISTRY OF 2,3-DI-n-PROPYL-1,4-DEHYDROBENZENE

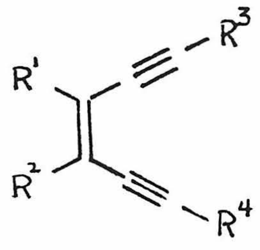
Introduction

As mentioned in Chapter I, there has been continuing interest in this laboratory in characterizing the reactivity of 1,4-dehydrobenzene. We wished especially to obtain conclusive evidence[6] that 1,4-dehydrobenzene is a discrete species of finite lifetime. Several approaches to test this hypothesis suggested themselves. The first was to generate 1,4-dehydrobenzene under conditions where it could be directly observed. A second method was to obtain kinetic evidence for the occurrence of 1,4-dehydrobenzene as a reactive intermediate on a pathway leading to observed products. Duncan Brown in this laboratory pursued a low temperature, photochemical route to the butalene/1,4-dehydrobenzene energy surface that was intended to allow the direct observation of these species.[20] My approach has involved a kinetic study of the generation of a substituted 1,4-dehydrobenzene by the thermal reaction of a diethynyl olefin.

There are several drawbacks to the use of diethynyl olefin **4** as a thermal precursor of 1,4-dehydrobenzene. The yield of aromatic products in solution pyrolyses of **4** is generally quite low (<50%).[6,21] In addition, the sensitivity of **4** toward air oxidation and rapid thermal polymerization (even at subambient temperatures) makes it rather inconvenient to work with. It was hoped that substitution of the diethynyl olefin framework would lead to improved stability at ambient temperature and to kinetic stabilization against adventitious side reactions during thermal reaction in solution. Ideally, the substituents should be ones that have an insignificant effect on the electronic structure of 1,4-dehydrobenzene.

Toward this end, a number of compounds (**20a-w**, Table 2) were prepared in this laboratory[22]. The thermal reactions of some of these molecules proved to be quite interesting.[9,23] These investigations indicated that alkyl and trimethylsilyl substituted diethynyl olefins are appreciably easier to work with than the unsubstituted compound, **4**, roughly in proportion to the number and steric bulk of the substituents. Unfortunately, only modest improvements in the yield of aromatic products were realized through these modifications. Substitution at the acetylenic carbons greatly raised the temperature required to effect cyclization to the substituted 1,4-dehydrobenzenes. This is an undesired effect, since more vigorous reaction conditions are expected to increase the mechanistic complexity. During these investigations an additional problem was identified: interaction of 1,4-dehydrobenzene biradicals with solvent molecules can produce free radicals which may subsequently attack unreacted diacetylene.

Observations by Charles Mallon of the interesting unimolecular thermal chemistry of compound **20n** prompted us to further investigate the chemistry of di-n-propyl substituted diethynyl olefins.[23] Compound **19** was identified as the most promising molecule to study; because of the unsubstituted acetylenic positions **19** was expected to rearrange at temperatures considerably lower than **20n**.[21]



20

Table 2. Diethynyl Olefins That Have Been Prepared in this Laboratory.

	R^1	R^2	R^3	R^4
20a	H	H	methyl	methyl
b	H	H	phenyl	phenyl
c	H	H	t-butyl	H
d	H	t-butyl	H	H
e	H	t-butyl	$SiMe_3$	H
f	H	t-butyl	$SiMe_3$	$SiMe_3$
g	H	ethyl	ethyl	H
h	H	n-propyl	n-propyl	H
i	H	ethyl	ethyl	$SiMe_3$
j	H	n-propyl	n-propyl	$SiMe_3$
k	methyl	methyl	H	H
l	methyl	methyl	methyl	methyl
m	methyl	methyl	n-propyl	n-propyl
n	n-propyl	n-propyl	methyl	methyl
o	methyl	methyl	phenyl	phenyl
p	t-butyl	$SiMe_3$	H	H
q	$R^1 = R^2 = -(CH_2)_4-$		methyl	methyl
r	"		n-propyl	n-propyl
s	"		phenyl	phenyl
t	$R^1 = R^2 =$ benzo		H	H
u	H	H	$SiMe_3$	$SiMe_3$
v	t-butyl	H	$SiMe_3$	$SiMe_3$
w	$SiMe_3$	H	$SiMe_3$	t-butyl

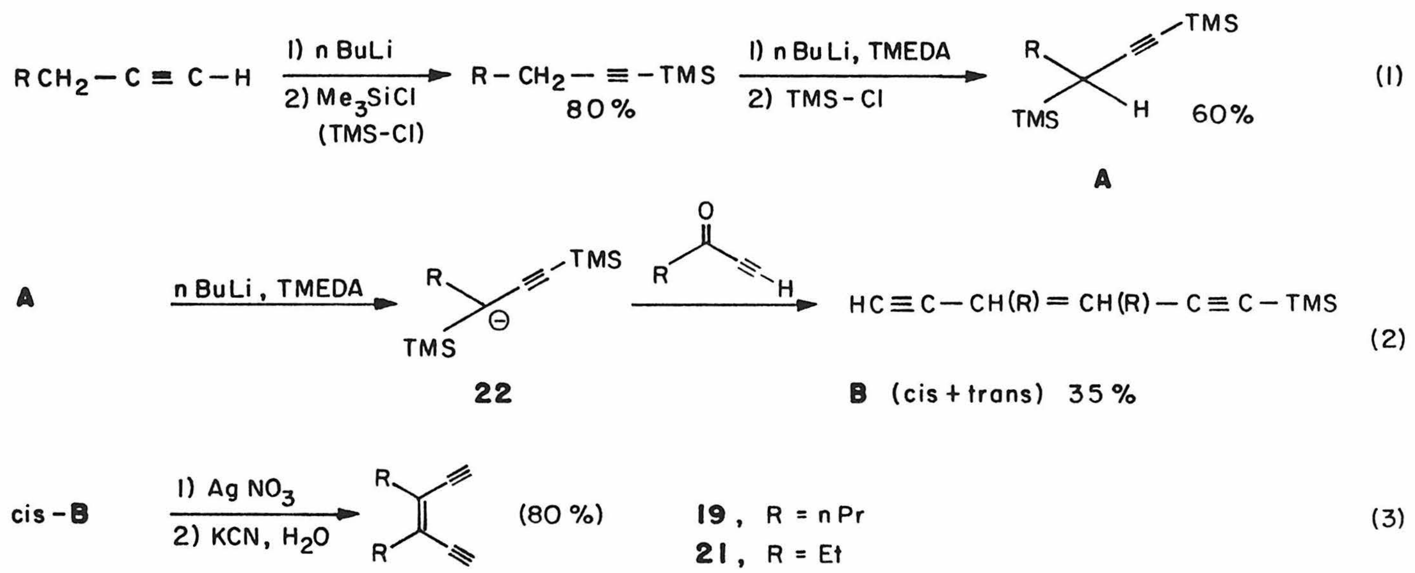
Results

Synthesis

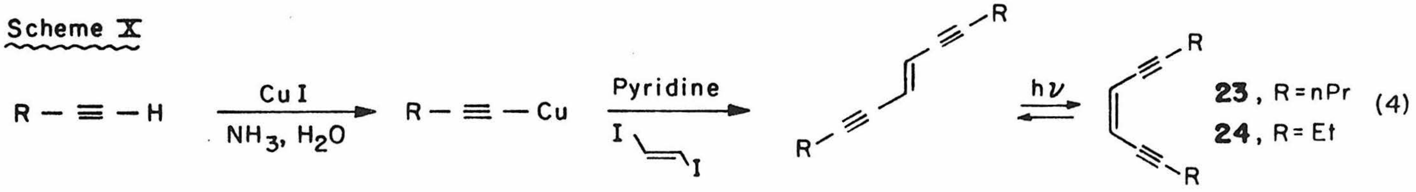
Four diethynyl olefins were prepared in the course of the mechanistic investigations reported in this section. Two contained alkyl substituents at both vinyl positions (**19**, **21**). The synthetic route to these compounds followed a general method previously employed by Gilbert Johnson and John Stofko in this laboratory (Scheme IX).[24] The key step (equation 2) is an olefination reaction by the method of Pederson, et al.[25] Anion **22** undergoes both addition to the carbonyl and acetylenic H abstraction; this led to only modest yields of the desired diethynyl olefins, which were produced in roughly a 40:60 ratio of cis and trans isomers. Separation of the isomers was conveniently effected by column chromatography on silica gel. Photolysis of the trans olefin in alkane solvents led to cis-trans isomerization. By this method the trans product of the olefination reaction was converted to a mixture (ca. 1:1) of the cis and trans isomers. Finally, removal of the acetylenic trimethylsilyl (TMS) group was accomplished in high yield by the method of Arens and Schmidt (equation 3).[26]

We also required two compounds, **23** and **24**, substituted at the acetylenic positions. Compounds of this type are most conveniently prepared by the coupling of copper acetylides[27] with trans-1,2-diiodoethylene[28] (Scheme X). Photoisomerization of the trans isomer followed by column chromatography gave the desired cis isomer.

Scheme IX



Scheme X



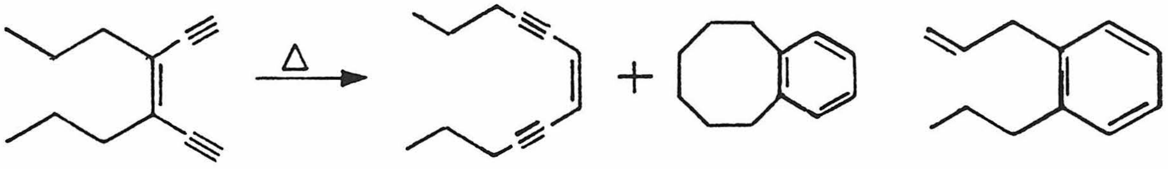
Although the diethynyl olefins obtained after chromatography on silica gel were >95% pure, before pyrolysis they were usually further purified by preparative gas chromatography. This method provided the diacetylenes in >99% purity. The neat diacetylenes could be handled briefly at room temperature in the air but yellow coloration appeared after several minutes under these conditions. When stored in solution (ca. 1-5% v/v) the lifetime of these compounds was greatly improved, although temperatures of -60° C were required to effectively eliminate discoloration due, presumably, to polymerization.

Thermal Reactions

Gas phase experiments were performed by passing the diacetylenes through a heated quartz tube either under a stream of N_2 (1 atm pressure) or at reduced pressure. The products were collected on a cold finger at -196° C. Solution reactions were carried out in sealed glass tubes. The concentration of the diacetylenes was usually 10^{-2} M or less and the samples were subjected to four freeze-pump-thaw cycles to remove oxygen.

Compound **19** was pyrolyzed in the gas phase and in a number of solvents. The thermal reaction of **19** in the gas phase (N_2 flow, 320° C) produced a quantitative yield of three products: isomeric diyne **23**, benzocyclooctene (**25**), and o-allyl-n-propylbenzene (**26**, Scheme XI). The three products were isolated by preparative VPC and characterized by their NMR, IR and high resolution mass spectra.[29] Compound **23** was identified

Scheme XI



19 **23** **25** **26**

27

additionally by independent synthesis. When **23** was heated in the gas phase at 400° C (N_2 flow, contact time ca. 1.5 min), greater than 95% conversion to **25** and **26** was observed.

We studied the thermal chemistry of **19** in solution in order to obtain accurate kinetic data for its cyclization. Aromatic solvents were expected to be unreactive toward free radical hydrogen atom abstraction and, indeed, proved to be almost completely inert toward the intermediates produced during the reaction of **19**. Heating **19** at 196° C for 15 minutes in diphenyl ether, chlorobenzene or benzene led to complete conversion of the starting material to **23**, **25** and **26** in high yield (Table 3). Notably, at this temperature diacetylene **23** was quite stable and did not react detectably. In addition to unimolecular products, several isomeric compounds (total yield <5%) of empirical formula $C_{18}H_{21}Cl$ were observed by VPC-mass spectroscopy (**27**). These compounds appear to be formed by addition of reactive intermediates to the solvent.

We also wanted to find a suitable trapping agent for the intermediate(s) produced in the reaction of **19**. First we investigated the reaction of **19** with simple alkanes and alkyl substituted aromatic solvents which, we reasoned, would effectively transfer hydrogen to biradical and radical intermediates. Unfortunately, the yield of tractable products was quite low (<40%) when these solvents were employed. The reacted solutions were badly discolored which suggests the occurrence of competitive polymerization reactions. Subsequently, we found that the addition of a small amount (<15%

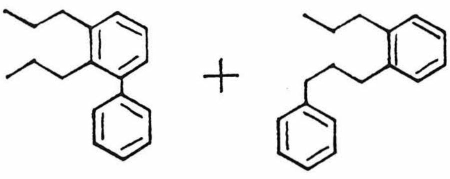
Table 3. Product Yields and Rate Constants in the Solution Pyrolysis of **19**.[a]

Run	T (°C)	k_{obs} (sec^{-1})	1,4-cyclohexadiene (M)	Absolute Yield (%)[b] 24	26	25	28	Total (24 - 28)
(1)	196	--	0.0	20.3	36.9	20.8	--	78
(2)	196	--	0.4	10.1	8.9	5.4	48	71
(3)	196	--	10.6	~1.0	<1	<1	76	<79
(4)	166	1.3×10^{-3}	0.0	13.5	38.5	20.0	--	72
(5)	156	6.9×10^{-4}	0.0	11.8	35.8	17.2	--	65
(6)	145	2.9×10^{-4}	0.0	9.8	37.3	17.6	--	65
(7)	132	9.3×10^{-5}	0.0	7.9	38.5	16.4	--	63
(8)	156	7.1×10^{-4}	0.19	8.7	13.5	8.7	27.6	58
(9)	156	6.4×10^{-4}	0.38	5.2	6.7	3.1	47.4	62

[a] [**19**] = 0.01 M

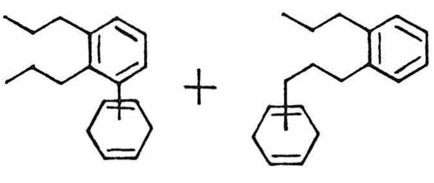
[b] Yields determined by digital integration of FID vpc trace and reference to an internal standard.

by volume) of a better hydrogen atom donor to solutions of **19** in one of the inert solvents produced a high yield of products. Both 1,4-cyclohexadiene and 9,10-dihydroanthracene were extremely effective as hydrogen donors; 1,4-cyclohexadiene was most convenient to use because of its solubility properities. In the presence of these trapping agents a new product, o-di-n-propylbenzene (**28**) was obtained in high yield. The yield of **28** increased with added trapping agent at the expense of the three unimolecular products (see Table 3, runs (1)-(3), and figure 1). Several higher molecular weight products (total yield roughly 1/4 that of **28**) were also observed in these pyrolyses. By VPC-mass spectroscopy these compounds were found to be isomers of molecular formula $C_{18}H_{22}$ (**29**) and $C_{18}H_{24}$ (**30**) and are believed to have the structures shown below. In addition, several products with the molecular formula $C_{12}H_{14}$ and $C_{12}H_{12}$ were formed in modest yield. These are believed to be dimers formed by the combination of cyclohexadienyl radicals.



$C_{18}H_{22}$

29



$C_{18}H_{24}$

30

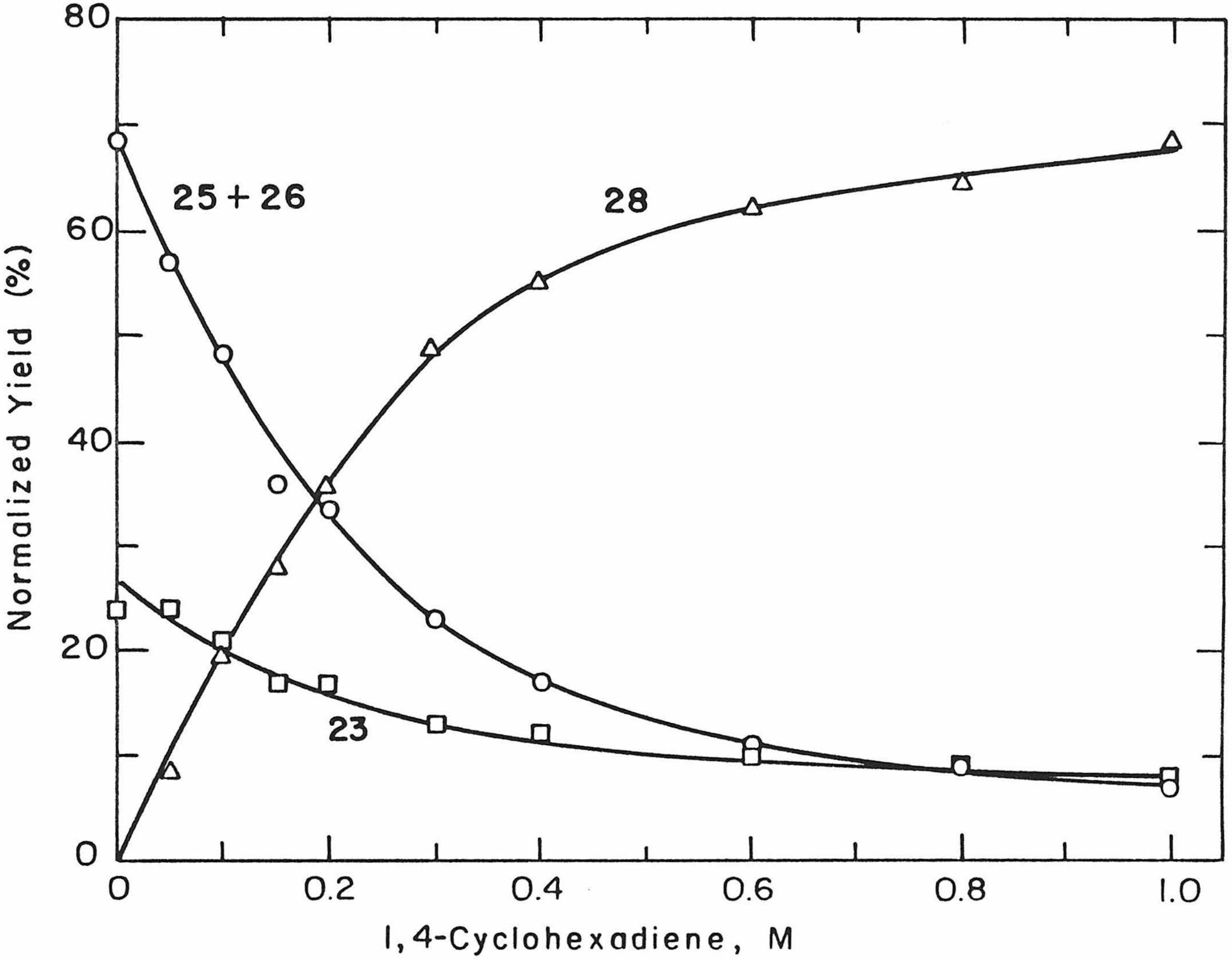


Figure 1. Plot of normalized product yields as a function of the amount of 1,4-cyclohexadiene in the reaction solution.

When 2,2,5,5-tetradeuterio-1,4-cyclohexadiene was employed as the trapping agent, the **28** formed contained two deuteria per molecule. The yield of tractable products in this reaction, however, was substantially lower than when undeuterated cyclohexadiene was used. This is believed to reflect reduced reactivity of the deuterated trap toward the intermediate biradicals.[30] When cyclohexadiene-d_4 was employed as trapping agent the high molecular weight products formed, **29** and **30**, contained 2 and 4 deuteria per molecule, respectively, as determined by mass spectroscopy. As expected, the unimolecular products formed showed no incorporation of deuterium. The location of deuterium in **28** was determined in the following way: using the method of Werstiuk and Kadai[31] the aromatic deuteria were selectively exchanged for protons through acid catalysis. After the exchange was completed, **28** was examined by mass spectroscopy and the molecular ions (corresponding to 0, 1 and 2 residual deuteria per molecule) were measured. The results indicate that, when **19** was heated in chlorobenzene with 1,4-cyclohexadiene-d_4 (0.8 M), 66% of the product **28** formed contained two aromatic deuteria, 33% contained one aromatic and one aliphatic deuteria and about 1% of product **28** contained two aliphatic deuteria. The ramifications of this result are discussed further in the next section (C).

The kinetics of disappearance of **19** in chlorobenzene solution (10^{-2} M) were measured both in the presence and absence of added cyclohexadiene (Table 3). Linear first order plots for three reaction half-lives were obtained at four temperatures spanning a range of 34° C. Clean first order kinetics were also observed for the reaction of **19** in 0.19 and 0.38 M solutions of 1,4-cyclohexadiene with chlorobenzene solvent. In the presence of added trapping agent, the reaction rate was unchanged within experimental error (Table 3, runs (5), (8) and (9)).

The thermal reactions of **21** and **24** in the gas phase were also investigated.[32] At temperatures below 425° C quantitative conversion of **21** to **24** was the only process observed. At higher temperatures additional unimolecular products appeared. The predominant products were o-ethylstyrene, tetralin, benzocyclobutene and styrene (Table 4). These products were also observed when **24** was allowed to react under similar conditions.

Thermal reaction of **21** in benzene solution (10^{-2} M, see Table 4) gave diacetylene isomer **24** plus a small amount of o-diethylbenzene, bibenzyl, and a product (**31**) of molecular formula $C_{16}H_{18}$ (identified by VPC-mass spectroscopy) whose structure is postulated to be that shown below. When **21** was heated at 190° C in a solution of benzene-d_6, o-diethylbenzene containing deuterium, in the ratio $d_0:d_1:d_2 = 3:3.4:1$, was formed, demonstrating that significant abstraction of deuterium from benzene took place. The bibenzyl produced was found to be fully deuterated and is believed to have been formed as a result of this reaction channel. The source of hydrogen is assumed to have been the diacetylenes **21** and **24** and the protio reaction products.

Reaction of **21** in a benzene solution containing 1,4-cyclohexadiene gave greatly reduced yields of unimolecular

Table 4. Product Yields in the Reaction of 21.

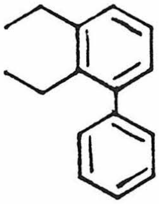
Run	Phase	T(°C)	Absolute Yield (%)[a]					
			24 (c + t)	styrene	benzo-cyclo-butane	o-allyl styrene	tetralin	o-di-ethyl benzene
(1)	gas[b]	400	100	0	0	0	0	0
(2)	gas[b]	500	76.8	1.3	7.8	8.8	1.6	0
(3)	benzene solution[c]	195	51	0	0	0	0	5
(4)	benzene + 1,4-cyclo-hexadiene (1.1 M)[c]	195	6	0	0	0	0	75

[a] Yields determined by digital integration of FID VPC trace and reference to internal standard

[b] N_2 flow

[c] [21] = 0.01 M

products; o-diethylbenzene was obtained in good yield (Table 4). Several high molecular weight products formed were detected by VPC-mass spectroscopy and have the molecular formula $C_{16}H_{20}$ (**32**).



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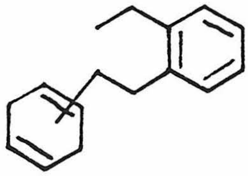

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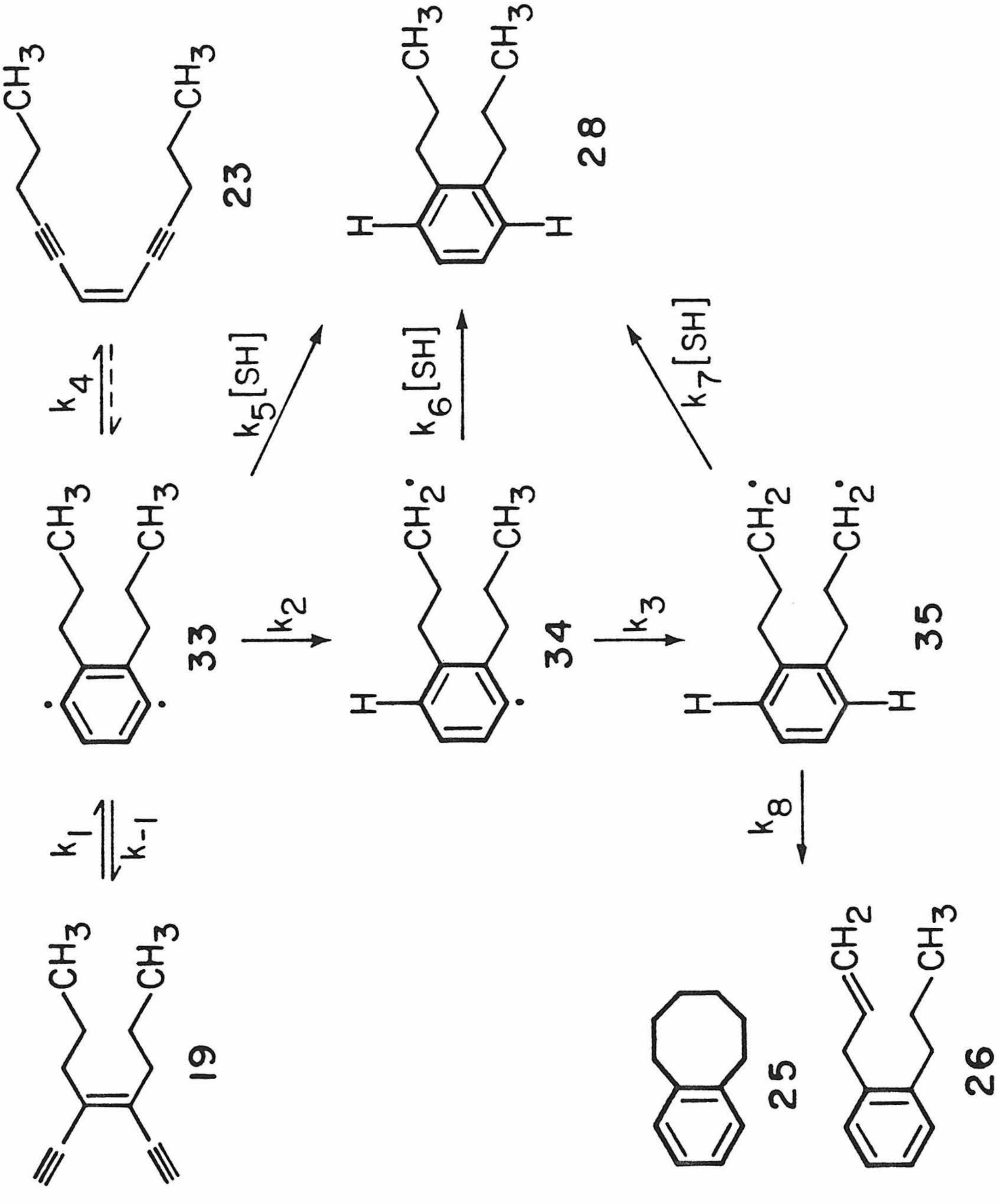
Discussion

Proposed Mechanisms

To account for the results obtained in the thermolysis of **19** we propose the mechanism outlined in Scheme XII which involves initial ring closure of **19** to produce the 2,3-di-n-propyl-1,4-dehydrobenzene biradical **33**. In the absence of trapping agent two unimolecular pathways are available to **33**. Ring opening to form rearranged diacetylene **23** (or return to the starting compound) may take place in analogy with the results observed by Jones and Bergman for the deuterium labelled diacetylene **4a** (Scheme III).[6] Additionally, biradical **33** may transfer hydrogen from the terminus of a propyl group to the nearest aromatic radical site to produce biradical **34**. This is expected to be a facile process since a kinetically favorable six-membered transition state is involved.[33] Furthermore, the heat of formation of biradical **34** is estimated to be about 12 kcal/mole less than that of **33**, the difference in strength of primary alkyl and aryl C-H bonds.[34] Ring closure in **34** to give a [3]metacyclophane is expected to be unfavorable as the smallest known [**n**]metacyclophane has a pentamethylene bridge, (**n** = 5) and rearranges to indane at 150^{o} C.[35] Instead, a second intramolecular hydrogen transfer to produce biradical **35** may take place. Unimolecular products **25** and **26** argue very forcefully for the presence of **35** on the reaction pathway and strongly suggest the location of the radical sites at the termini of the n-propyl substituents. In fact, the failure to observe smaller ring

Scheme XII

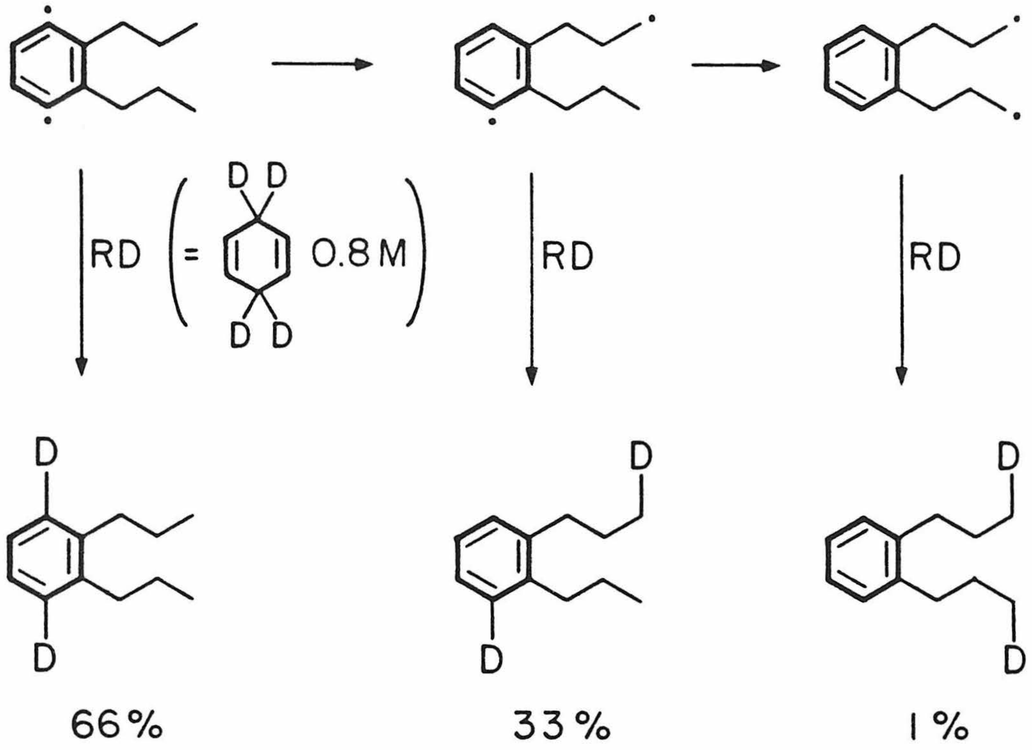

19
33
23
34
28
35
25
26
k_1
k_{-1}
k_2
k_3
k_4
$k_5[SH]$
$k_6[SH]$
$k_7[SH]$
k_8
CH_3
$CH_2^{\cdot}$
CH_2
H

benzocycles or o-propyl-β-methylstyrene argues against the occurrence of other intramolecular hydrogen transfer modes (ie. [1,4]) in **33** or **34**.

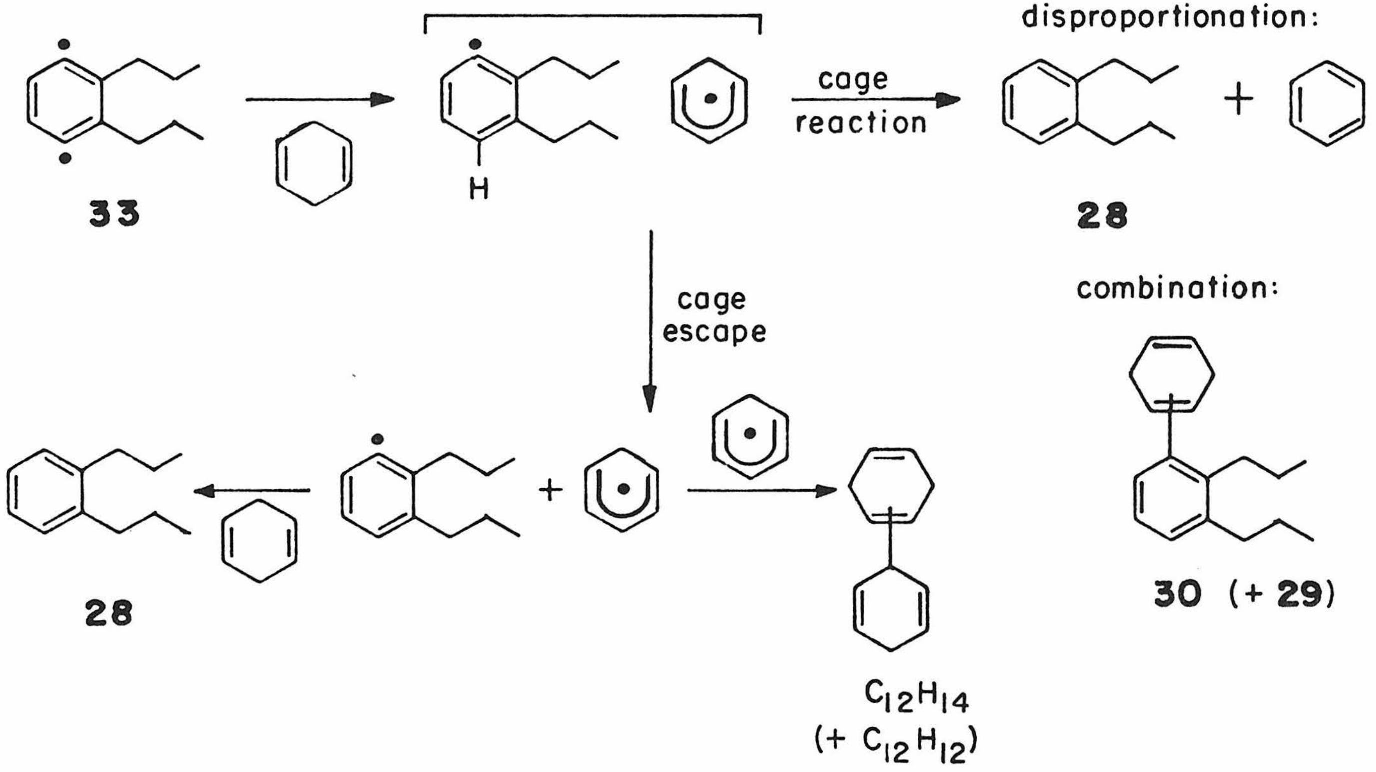
The presence of 1,4-cyclohexadiene in the reaction solution leads to the formation of **28** which may in principle come from trapping of any of the three biradical intermediates. The results of the deuterium labelling study mentioned previously (see the Results section) indicate that trapping occurs predominantly from biradicals **33** and **34** (Scheme XIII). Only 1% of **28** formed was found to contain two deuteria in the alkyl side chains when the pyrolysis solution was 0.8 M in cyclohexadiene-d_4.

The formation of high molecular weight products in the solution pyrolyses of **19** is readily understood in terms of the proposed mechanism. Product **27** appears have been formed from attack on the chlorobenzene solvent by intermediate biradicals **33** and **34**. By our mechanism (Scheme XIV), transfer of hydrogen from cyclohexadiene to one of the biradical intermediates generates a radical pair; transfer of a second hydrogen within the solvent cage led to the **28** formed. Cage escape may also have led to the formation of **28**. Combination of cage-escaped cyclohexadienyl radicals appears to have been responsible for the formation of products with the molecular formula $C_{12}H_{14}$ and $C_{12}H_{12}$ (in the reaction with cyclohexadiene-d_4 these products have new molecular weights corresponding to $C_{12}D_{12}$ and $C_{12}D_{14}$). Cage combination of the radical pair may be responsible for the several isomers with

Scheme XIII



Scheme XIV

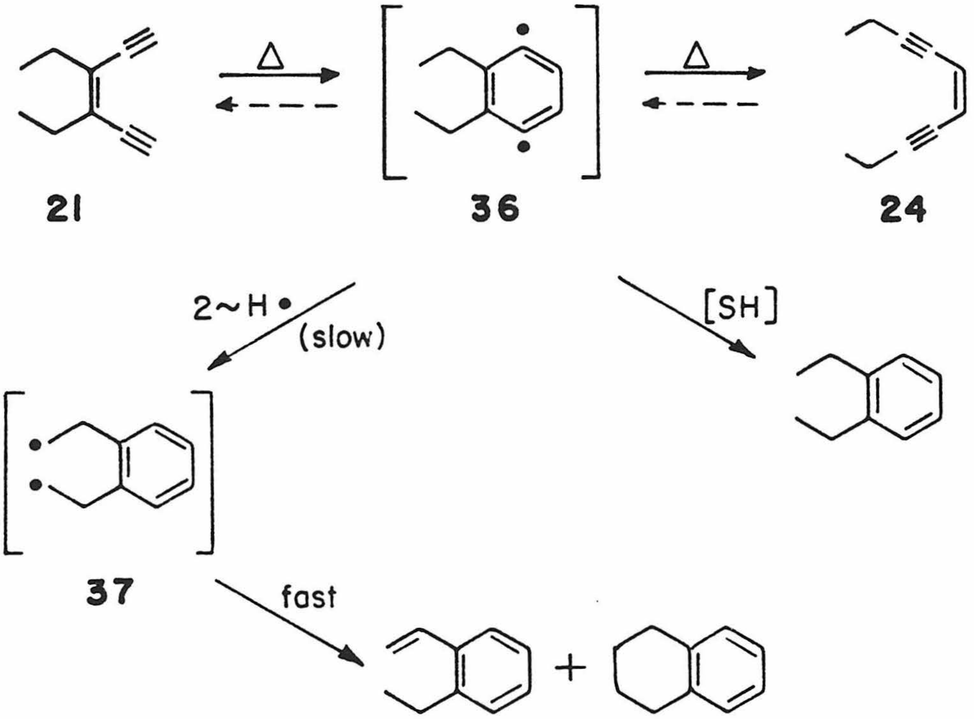

33
H
cage
reaction
disproportionation:
28
combination:
30 (+ 29)
cage
escape
28
$C_{12}H_{14}$
(+ $C_{12}H_{12}$)

the formula $C_{18}H_{24}$ (**30**) found. Hydrogen loss from some of these combination products (either under the reaction conditions or in the mass spectrometer) accounts for the formation of products of formula $C_{18}H_{22}$ (**29**) observed. Supporting the identification of **29** and **30** are the observations that (1) these compounds only appeared in reaction solutions containing cyclohexadiene; (2) the yields of **29** and **30** were directly related to the yield of trapping product **28**; (3) mass spectral fragmentation gives large peaks due to the phenyl cation, cyclohexadienyl radical cation and dipropylbenzene cation ($C_{12}H_{18}$); and (4) when cyclohexadiene-d_4 was used, **29** was formed containing two deuteria per molecule, **30** with four deuteria per molecule.

It is informative to consider here the results of the thermal reactions of diacetylenes **21** and **24** (Table 4). The products obtained in the gas phase and in solution pyrolyses in benzene suggest the mechanism presented in Scheme XV. Intermediate **36** appears to undergo intramolecular [1,4] hydrogen transfer slowly relative to ring opening to diacetylene **21** or **24**. Thus, **21** may be converted quantitatively to **24** in the gas phase (400° C) without appreciable intramolecular trapping of the 1,4-dehydrobenzene intermediate. Only at much higher temperatures (<u>ca</u>. 500° C), where **24** is repeatedly converted to **36**, were products of intramolecular hydrogen transfer found.[36]

In benzene solution **21** was similarly converted to **24**. No intramolecular hydrogen transfer was observed, though in the presence of added cyclohexadiene the 1,4-dehydrobenzene intermediate was efficiently trapped to give o-diethylbenzene.

Scheme XV



At the temperatures employed in the solution studies, the rearrangement of **36** to **24** is essentially irreversible. Each molecule of **21**, therefore, can generate **36** only a single time in the course of this reaction. Our failure to detect even trace amounts of tetralin or o-ethylstyrene indicates that the rate of [1,4] hydrogen transfer must be several orders of magnitude slower than ring opening to **24**.

We may reasonably assume that the rate of rearrangement of **36** to **24** is comparable to that of **33** rearranging to **23**. This provides a reasonable explanation for the failure to detect [1,4] hydrogen transfer in **33**, where [1,5] transfer is faster than ring opening to **23**.

Kinetic Studies

In accord with the mechanism presented in Scheme XII, the disappearance of **19** shows first-order kinetics. From the rate data measured over a 34° C range, the activation parameters for the first step in the reaction mechanism can be determined from an Arrhenius plot (figure 2, $E_a = 27.4 \pm 0.5$ kcal/mole and $\log_{10}A = 10.8 \pm 0.3$ sec^{-1}).

The Arrhenius parameters obtained for the reaction of **19** are valid only if the return of 1,4-dehydrobenzene **33** to **19** (k_{-1}) is slow with respect to the other reaction rates (k_4, k_2, k_5[SH]). We may determine the importance of k_{-1} and obtain kinetic evidence for the intermediacy of **33** by testing the following hypothesis: if biradical **33** is a true intermediate on the

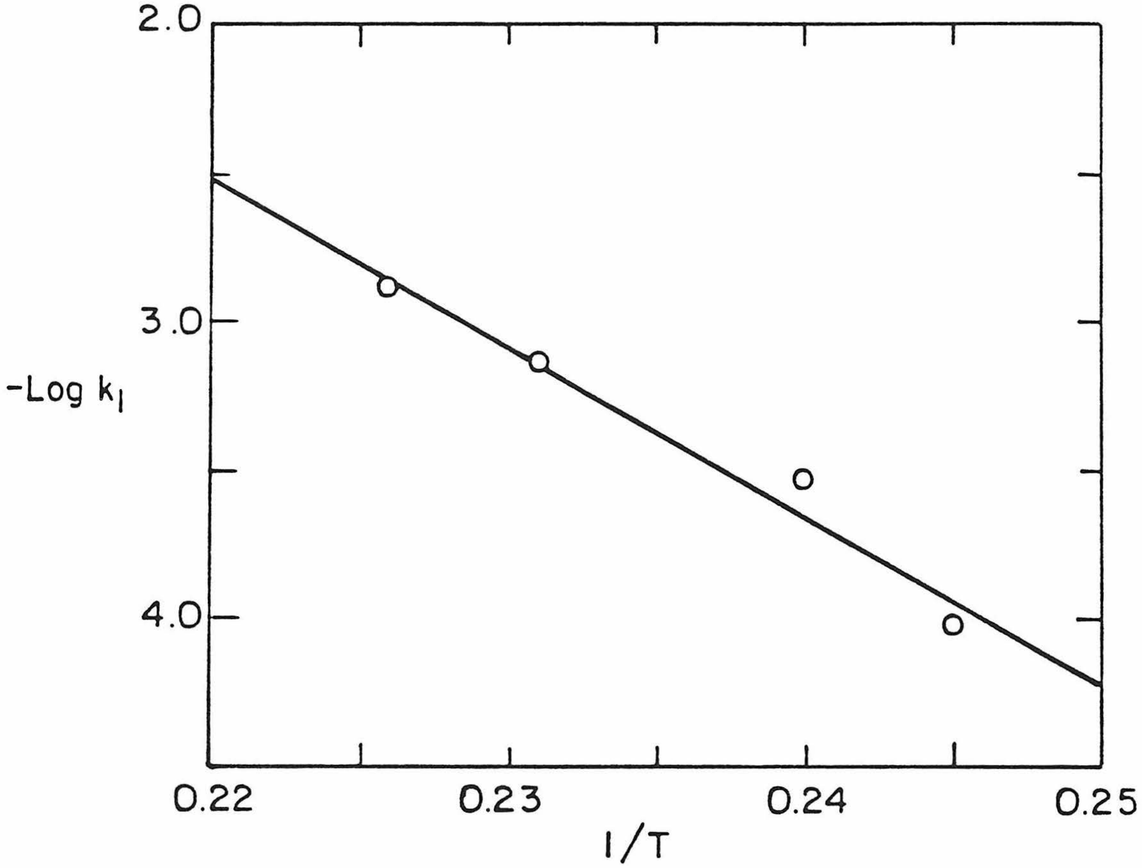


Figure 2. Arrhenius plot of unimolecular rate constants observed in the reaction of 19 (0.01 M) in chlorobenzene.

reaction pathway leading from **19** to products, and if the unimolecular rate constants (k_4 and k_2) and the bimolecular rate constant (k_5[SH]) are rapid with respect to k_{-1}, then the rate of disappearance of **19** must be independent of the presence of cyclohexadiene in the reaction solution. However, the product distribution will be dependent on the cyclohexadiene concentration if **33** is an intermediate and k_5[SH] is of comparable magnitude to the unimolecular reaction rates. The rate constants obtained, when 0.19 and 0.38 M added 1,4-cyclohexadiene were heated with **19** at 156° C, are identical, within experimental error, to that obtained in the absence of trapping agent (Table 3, runs (5), (8) and (9)). As predicted by our mechanism, while the rate of reaction of **19** was unchanged, the increase in cyclohexadiene concentration changed the yield of **28** from 0 to 47%.

The mechanism in Scheme XII makes several other specific predictions about the dependence of product yields on the concentration of trapping agent in the reaction solution. Application of the steady-state approximation to the concentration of **33** gives equation (5). Scheme XII predicts that the yield of **23** will be inversely proportional to the concentration of 1,4-cyclohexadiene (equation (5)). The experimental data are plotted in figure 3 and show good agreement with the mechanism proposed.

$$(\text{normalized yield of } 23)^{-1} = 1 + \frac{k_2}{k_4} + \frac{k_5\,[\text{SH}]}{k_4} \qquad (5)$$

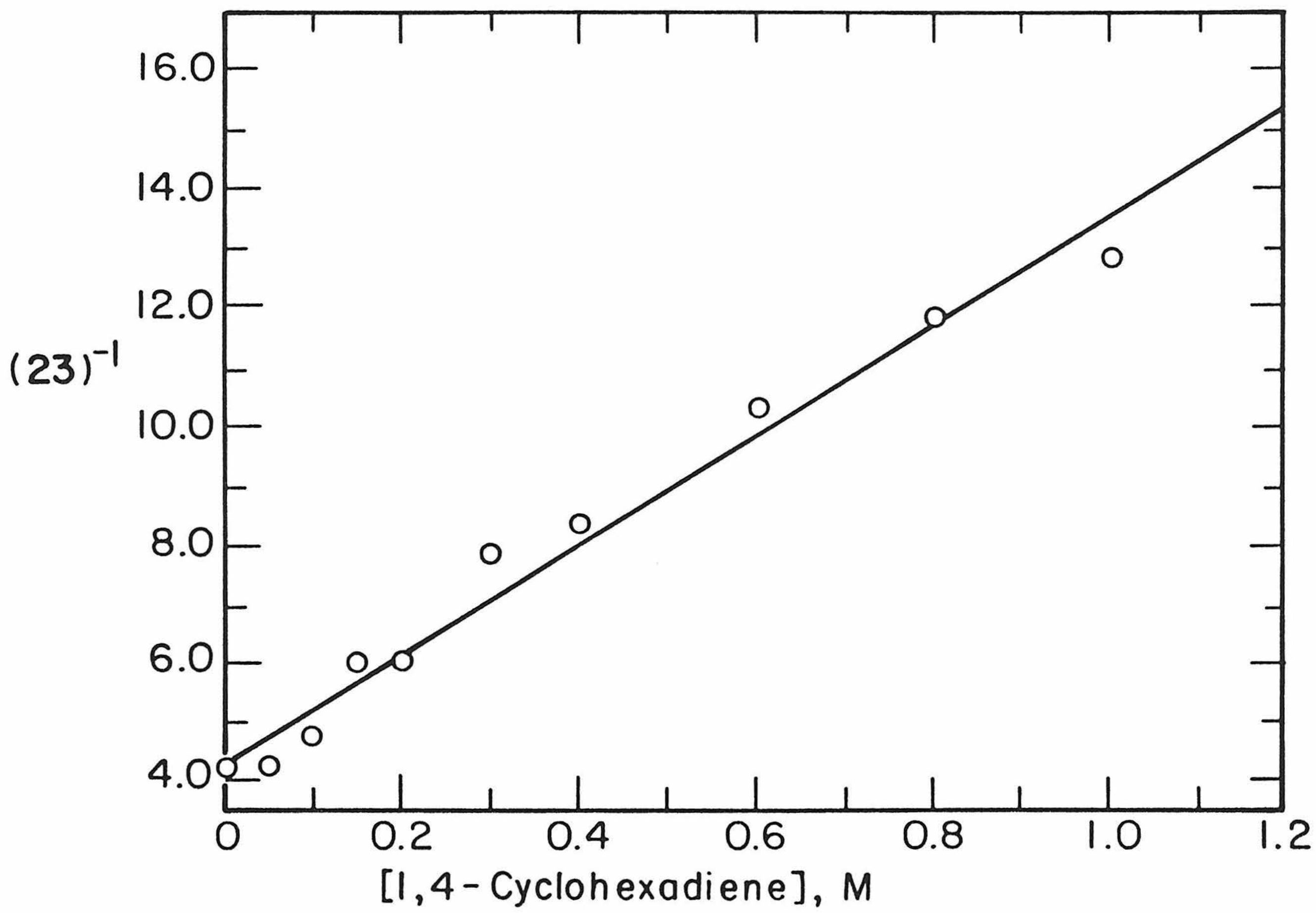


Figure 3. Plot of (normalized yield of 23)$^{-1}$ versus concentration of 1,4-cyclohexadiene. Conc. 19 = 0.01 M, T = 190° C.

The absolute yields of the unimolecular products **23**, **25** and **26** are strongly dependent on the concentration of trapping agent (figure 1). The yields of **25** and **26** show a more pronounced decrease upon the addition of cyclohexadiene than does the yield of **23** (the ratio **25**/**26**, however, remains constant). We may explain the nature of this dependence using the proposed mechanism if we make use of the following simplifying assumption: from experiments with cyclohexadiene-d_4 we know that a negligible amount of **28** arises from trapping of biradical **35**. Therefore, $d[\mathbf{25} + \mathbf{26}]/dt = k_3[\mathbf{34}]$. Equation (7) follows from equation (6) by application of the steady state approximation to intermediates **33** and **34**.

$$\frac{\text{Yield of 23}}{\text{Yield of 25 + 26}} = \frac{k_4(33)}{k_3(34)} \tag{6}$$

$$\frac{\text{Yield of 23}}{\text{Yield of 25 + 26}} = \frac{k_4}{k_2} + \frac{k_4\ k_6\ [\text{SH}]}{k_2\ k_3} \tag{7}$$

Equation (7) relates the ratio of **23** to **25** and **26** as a function of added cyclohexadiene. The linear plot obtained by applying this function to the experimental data (figure 4) confirms the existence of a second intermediate which undergoes trapping with cyclohexadiene (in agreement with the cyclohexadiene-d_4 experiments). The intercept of that plot gives the value of k_4/k_2 as 0.36 ± 0.01; this is the ratio of unimolecular products in the absence of added trapping agent. Similarly, dividing the slope of the line by the intercept gives the ratio k_6/k_3 as 2.0 M^{-1}. Since the intercept of the line

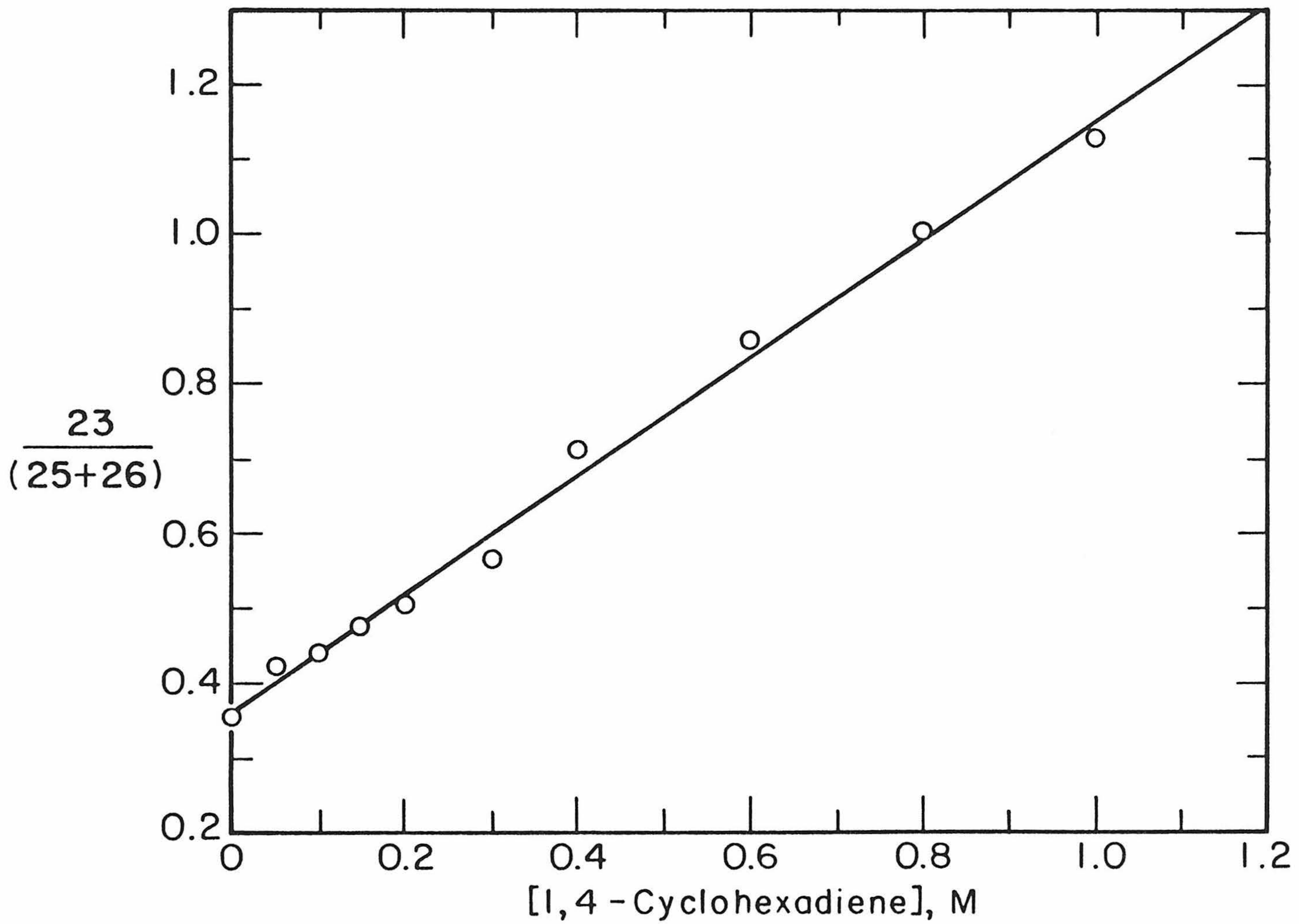


Figure 4. Plot of the ratio of the observed yields of 23/(25 + 26) as a function of 1,4-cyclohexadiene concentration. Concentration of 19 = 0.01 M, T = 190° C.

agrees with the ratio of unimolecular products observed in the absence of trapping agent (0.35), the presence of cyclohexadiene does not significantly affect the reaction rates at the concentrations studied.

CIDNP

We also have obtained good evidence for the presence of a third biradical on the reaction pathway of **19**. When a solution of **19** in o-dibromobenzene or diphenyl ether was heated at 160° C in the probe of an NMR spectrometer, several emissive signals were observed (figure 5). These signals are assigned to the vinyl protons and, tentatively, to the alkyl protons (terminal methyl and methylene) in polarized **26**. The observation that only polarization of the hydrogens at the two end carbons of the propyl and propenyl chains occurred, and that all enhancements were emissive strongly implicate biradical **35** as the polarizing species. Thus, although 1,4-cyclohexadiene is not sufficiently reactive to trap biradical **35** to an appreciable extent, the CIDNP process is rapid enough to provide evidence for the presence of that intermediate.[37]

Summary of Arguments in Support of the Proposed Mechanism

It may be helpful at this point to summarize the evidence supporting the mechanism proposed in Scheme XII: (1) the formation of diacetylene **23** from **19** and the observation that **23** also rearranged at higher temperatures to generate products **25**

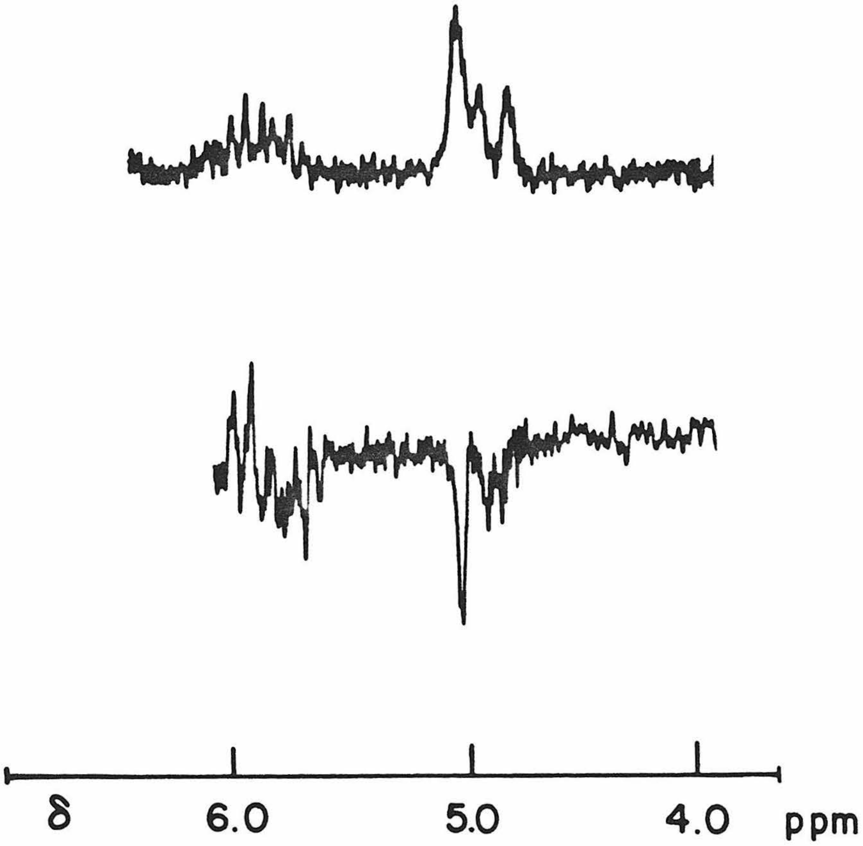


Figure 5. The upper spectrum (90 MHz ^1H) shows the vinyl region of a purified sample of o-allyl-n-propylbenzene recorded at 30° C. The lower spectrum shows the emissive signals observed during reaction of **19** at 160° C in a 90 MHz NMR probe. The signals appearing in absorption on the left side of the lower spectrum are spinning side bands of the solvent (o-dibromobenzene).

and **26** argues for an intermediate or transition state with the symmetry of 1,4-dehydrobenzene **33**.[6] (2) The yield of **23** was substantially reduced by added trapping agent while the decomposition rate of **19** was unaffected. The dependence of the yield of **23** on added 1,4-cyclohexadiene displayed the behavior expected if the 1,4-dehydrobenzene exists as an intermediate of finite lifetime. Together these observations establish the formation of 1,4-dehydrobenzene intermediates in the thermal reaction of diethynyl olefins. (3) The observation that two **28**-d_2 isomers were formed when cyclohexadiene-d_4 was used as a trapping agent indicates the presence of at least one additional intermediate. Experiments, which showed that one isomer was labelled at both the aromatic ring and the aliphatic side chain, support the postulate that **34** is formed in the reaction. Kinetic evidence for the second intermediate was also obtained by examining the ratio of unimolecular products formed as a function of added cyclohexadiene. (4) The reactivity of **33** and **34** (hydrogen abstraction from 1,4-cyclohexadiene, followed by combination and disproportionation) and intramolecular hydrogen transfer to produce biradical **35** clearly demonstrate the biradical nature of the intermediates. (5) Products **25** and **26** strongly suggest intramolecular combination and disproportionation from a common biradical precursor. The observation of CIDNP in **26** confirms the intermediacy of biradical **35**.

Estimated Absolute Rate Constants and Reaction Energetics

It is possible to estimate the absolute rate constants and activation energies for the reactions steps in Scheme XII. A reasonable model for cyclohexadiene trapping of **34** is the rate constant for abstraction of hydrogen from diphenylmethane by phenyl radicals (estimated to be 7.7×10^6 M^{-1} sec^{-1} at 60° C).[38] The unimolecular rate constants k_2, k_3 and k_4 are thus expected to lie between 10^6 and 10^7 sec^{-1} at 60° C; k_8 must be at least one or two orders of magnitude slower (vide supra).

A marked dependence of the ratio **23** /(**25** + **26**) on the reaction temperature is observed (Table 3, runs (1), (4), (5), (6) and (7)). This is convincing evidence that at least one of the intramolecular processes leading from **33** is activated. The difference in activation energies and A factors of the steps involving k_4 and k_2 can be obtained by a plot of ln[**23**/(**25** + **26**)] versus 1/T (equation (8)). A linear relationship is observed over a range of 64° C (figure 6); from the slope of the line the difference in activation energies, $E_a(k_4) - E_a(k_2)$ was found to be 5.2 ± 0.4 kcal/mole. The ratio $A(k_4)/A(k_2)$ was determined from the intercept to be 10^2. The E_a for [1,5] hydrogen transfer in **33** should be similar to that for the exothermic [1,5] hydrogen transfer observed in the 2,2-dimethylpentoxyl radical ($E_a = 5.0$ kcal/mole).[39] The conversion of **33** to **23** should therefore have an E_a of about 10 kcal/mole. The absolute magnitude of the A factor for the rearrangement of **33** to **34** may also be of similar magnitude to that of the rearrangment of the 2,2-dimethylpentoxyl radical ($10^{11.5}$ sec^{-1}). This seems reasonable since $A(k_4)$ is consequently predicted to be $10^{13.5}$ $\sec^{-1}$, an appropriate magnitude for the ring opening reaction.

$$\ln \frac{23}{25 + 26} = \ln \frac{A_2}{A_4} + \frac{E_a(k_4) - E_a(k_2)}{RT} \qquad (8)$$

Surprisingly, perhaps, a small temperature dependence was also observed on the relative yields of **25** and **26**. Treatment of the yield of **25** versus **26** as in equation (8) gives a linear plot from which the difference in the activation energies leading to **25** and **26** is found to be 1.6 kcal/mole, favoring rearrangement to **26**. The ratio of the frequency factors favors rearrangement to **25** by a factor of 3. The absolute magnitudes of the activation energies for ring closure and disproportionation of biradical **35** are expected to be very close to zero, and certainly less than 5 kcal/mole. We may combine the activation energies estimated above with group additivity estimates of the heats of formation[34] of the discrete molecular species in Scheme XII to produce an energy surface for the reaction of **19** (figure 6).[40] The activation enthalpy predicted by the energy diagram for the reaction of **19** to give **33** is 27.4 kcal/mole (experimental) while the value for the conversion of **23** to **33** is predicted to be 24 kcal/mole. It has been observed experimentally that in order to obtain a rate of rearrangement of **23** equal to that of **19**, much higher temperatures are required. The difference in reactivity must be due to a difference in A factors.[40] The most convenient

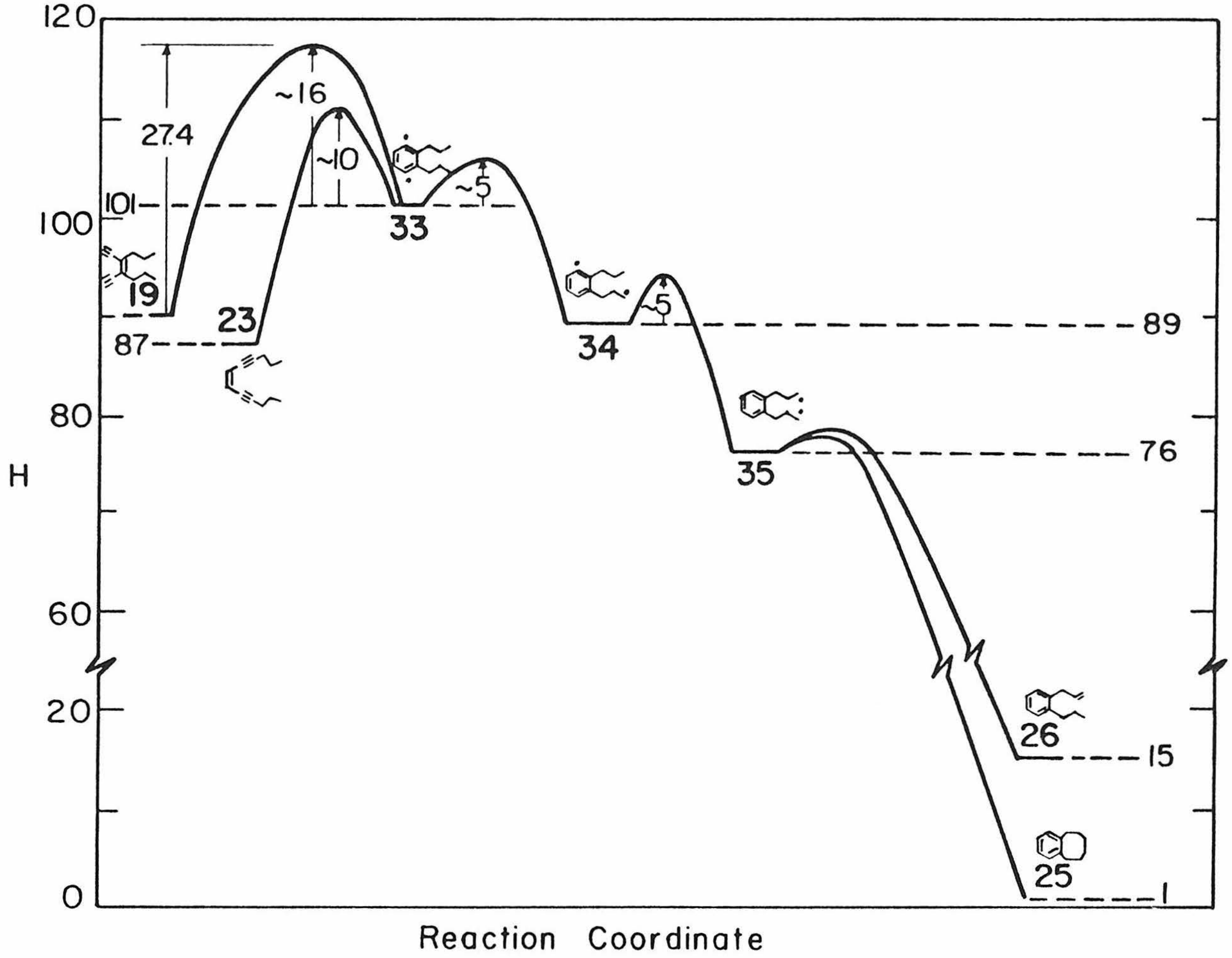


Figure 6. Enthalpy diagram for the reaction of 19 (all units in kcal/mole).

explanation of this difference is that alkyl substitution at the acetylenic positions lowers the frequency factor for cyclization due to steric crowding in the transition state.

Conclusions

In Chapter II we have presented observations that constitute strong support for the mechanism outlined in Scheme XII, and that provide information about the relative rates of the fast reactions of intermediates formed in the thermal reaction of **19** at elevated temperatures. The question concerning the reactive spin state of di-n-propyl-1,4-dehydrobenzene, remains to be addressed. Our efforts in this area are presented in Chapter III of this dissertation.

In relating the data obtained for **33** to the parent 1,4-dehydrobenzene, **3**, it seems reasonable to postulate that 1,4-dehydrobenzene lies in an energy minimum as does **33**. The absence of an intramolecular hydrogen transfer pathway such as that available to **33** should make the fastest reaction channel available to 1,4-dehydrobenzene the ring opening back to diacetylene **4**. The barrier to ring opening is likely to be within the range observed for opening of **33** to **19** and **23** (ca. 10 and 16 kcal/mole, respectively) and $\log_{10}A$ is probably on the order of 13. The short lifetime predicted for 1,4-dehydrobenzene by this analysis stands in sharp contrast to the observations reported by Berry, et al.[5] (Chapter I). They claim to have generated 1,4-dehydrobenzene photochemically and, on the basis of time-of-flight experiments, reported it to have a lifetime in excess of two minutes under their reaction conditions. Assuming the activation parameters for 1,4-dehydrobenzene suggested above, their estimate of the lifetime of **3** is at least several orders of magnitude too large. Their failure to detect evidence for the formation of diethynyl olefin **4** further suggests that 1,4-dehydrobenzene was not, in fact, generated under their experimental conditions.

A final question that needs to be addressed is whether or not the data presented here rule out the possibility that the lowest energy state of 1,4-dehydrobenzene may correspond to the bicyclic butalene structure. While the reactivity demonstrated by the 1,4-dehydrobenzene intermediate **33** is clearly that of a biradical, the possibility that a bicyclic ground state may be in equilibrium with the biradical or that the reactivity of butalene may be identical with the reactivity expected of the 1,4-biradical cannot be rigorously ruled out. The only other argument which bears on this point is that theoretical treatments have found the biradical structure to be substantially higher in energy than the "open" or biradical form.

Experimental Section

General

Pyridine was distilled from CaH_2 after heating at reflux for several hours. Dry diethyl ether was obtained from a commercial source (Mallinckrodt, anhydrous) and was used fresh from the container without further purification or drying. Absolute ethanol was also commercially available and was used without further purification. Reagent grade petroleum ether (bp 35-60° C) was purified by passing it through a column of activity I Alumina. Pyrolysis solvents were purified by repeated fractional distillation through a glass helices-packed column until only trace amounts of impurities (<0.1%) were detected by analytical VPC.

IR spectra were obtained on a Perkin-Elmer Model 237 or model 257 grating spectrophotometer. ^1H-NMR spectra were recorded on an EM-390 spectrometer. Chemical shifts are expressed in ppm downfield from tetramethylsilane. High resolution mass spectra (HRMS) were obtained on an AEI-MS12 spectrometer. VPC-mass spectral (VPC-MS) analyses were carried out using a Finnigan 4000 GC-mass spectrometer.

Elemental analyses were performed by the Microanalytical Laboratory, operated by the College of Chemistry, University of California, Berkeley, California.

Melting and boiling points are reported uncorrected.

Preparative VPC was performed on a Varian 90P instrument. Analytical VPC was conducted on either a Perkin-Elmer 3920 or a

Perkin-Elmer Sigma 3 chromatograph. Both were equipped with flame ionization detectors (FID) and were interfaced with a Spectra Physics Autolab System 1 computing integrator. The VPC columns used in the work reported here were the following: for preparative VPC-Column A: 10' x 1/4" glass 10% SF-96 on 60/80 Chrom W; Column B: 12' x 1/4" glass 10% SE-30 on 60/80 Chrom W-AW/DMCS; for analytical VPC- Column C: 9' x 1/8" stainless steel 10% SF-96 on 100/120 Chrom W-AW/DMCS; for VPC-MS analyses- 30 m glass capillary SP2100 wall coated open tubular (WCOT) column.

Gas phase pyrolyses were performed with a Hoskins Manufacturing Company Type FD 303A Electric Furnace. The pyrolysis tube was made of quartz tubing 35 cm long x 12 mm diameter and was fitted with 14/20 outer joints on the end. Flow pyrolyses were performed by passing a stream of N_2 gas over a magnetically stirred sample of the material to be heated; the gas flow was then passed through a liquid N_2 cooled trap and finally through a meter with which the flow rate was determined. Vacuum pyrolyses were performed with the same apparatus except that a vacuum (regulated by a manostat) was applied after the cold trap. Because of low volatility, the compounds studied were usually heated gently in order to increase their vapor pressure.

Solution pyrolyses were performed in the following way: the diethynyl olefins were isolated >99% pure by preparative VPC and promptly dissolved in the pyrolysis solvent in order to prevent discoloration due to polymerization. The solutions were syringed into hexamethyldisilazane treated glass tubes fitted with 14/20 female joints. After four freeze-pump-thaw cycles (to 0.02 torr) the tubes were sealed under vacuum. Samples for the CIDNP experiment were prepared in the same way except that NMR tubes fitted with 14/20 female joints were used, and the hexamethyldisilazane treatment was eliminated. Solutions were allowed to react by submersing them in an oil bath heated to the desired temperature. The concentration of the diacetylenes was determined by comparing the integrated peak area observed by FID-equipped VPC with the area of a known amount of an internal standard which had been added to the solution. The internal standards were n-alkanes of carbon number similar to the starting diacetylene. The error in the diacetylene concentration estimated by this method is expected to be small. The yield of unimolecular products was determined using the assumption that the response factors of compounds of the same molecular formula are equal.[41] The yield of higher molecular weight products was estimated by assuming that the response factors of these hydrocarbons, relative to those of the unimolecular products, was proportional to the number of carbon atoms in each.[41]

Samples for kinetic experiments were prepared in the same manner. The reaction temperature was controlled by submersing the reaction tubes in a vigorously refluxing solvent (eg. bromobenzene, bp = 156° C). Care was taken to minimize the contact of the sample tube with the walls of the solvent flask since this could have introduced an error into the reaction temperature. Data points were derived from the mean value of three VPC analyses of each sample.

Syntheses

The synthetic schemes employed in the preparation of the pairs of diacetylenes **19** and **21**, and **23** and **24**, were identical. Procedures are described in detail for the syntheses leading to **19** and **23**. Only the properties of the corresponding intermediates leading to **21** and **24** are given.

Propyl ethynyl ketone and ethyl ethynyl ketone: These compounds were prepared by the method of Bowden, et al.[42] Propyl ethynyl ketone: Bp = 52-53° C at 45 torr (literature[42]: Bp = 65-66° C at 100 torr). ^{1}H-NMR ($CDCl_3$): δ 0.95 (t,3H,J=7), 1.67 (sextet,2H,J=7), 2.52 (t,2H,J=7), 3.20 (s,1H). Ethyl ethynyl ketone (a strong lachrymator and sternutator) was isolated in 58% yield. Bp = 108-110° C at 1 atm. ^{1}H-NMR ($CDCl_3$): δ 1.12 (t,3H,J=8), 2.56 (q,2H,J=8), 3.15 (s,1H). IR (thin film): 3260 (acetylenic C-H stretch), 2790-2990 (alkyl C-H stretch), 2090 (C-C triple bond stretch), 1690 cm^{-1} (carbonyl). This compound was too easily air oxidized to allow satisfactory elemental analysis; the HRMS, however, was obtained: molecular weight calc. for C_5H_6O = 82.0419; found 82.0422.

1-Trimethylsilylhexyne: To an oven-dried 1 L three-neck flask fitted with two addition funnels, a condenser cooled to 5° C and an N_2 inlet was added 500 mL anhydrous ethyl ether and 1-hexyne (30 g, 0.37 mol). The solution was cooled to -20° C under an atmosphere of N_2 and stirred rapidly with a magnetic stirring bar. 165 mL of a 2.42 M (0.40 mol) hexane solution of nBuLi was added over 1 h. After addition the solution was allowed to warm to r.t. over 1 h. A white ppt. (the alkynyl lithium salt) rapidly formed. The solution was cooled to -20° C and trimethylsilyl chloride (45.7 g, 0.42 mol) was added over 20 min. Reaction was complete after the solution was stirred at r.t. for 4 h. The reaction was worked up by pouring 400 mL H_2O into the flask and then separating the mixture. The aqueous phase was washed with 250 mL ethyl ether. The combined organic phases were washed with 150 mL H_2O and then dried over Na_2SO_4. The ethyl ether solution was concentrated on a rotary evaporator and the product was isolated by fractional distillation through a Ta wire column. The product was obtained as a colorless liquid, bp 70-71° C (35 torr); isolated yield 44.1 g (77%), 99% pure (by VPC analysis). The NMR and bp agreed with those reported in the literature.[43]

1-Trimethylsilylpentyne: The isolated yield was (see preceding preparation), 38g, 74% (96% pure by VPC). Bp 55-57° C at 35 torr. The physical properties agreed with those reported in the literature.[44]

1,3-__Bis__(trimethylsilyl)hexyne: An oven dried 500 mL three neck flask was fitted with two addition funnels and an N_2 inlet. 200 mL anhydrous ethyl ether and 15.4 g (0.10 mol) 1-trimethylsilylhexyne were added and stirred magnetically at -20° C under an N_2 atmosphere. nBuLi (45 mL of a 2.42 M hexane solution, 0.11 mol) was added over 15 min followed by TMEDA (11.6g, 0.10 mol). The solution was stirred for 2 h at -20° C and then for 1 h at 10° C. After cooling the solution to -20° C again trimethylsilyl chloride (12.0 g, 0.11 mol) was added over

15 min. A white ppt (LiCl) formed immediately. The reaction solution was stirred for 1 h at -20° C and then warmed to r.t. for 1 h. To work up the reaction, 100 mL H_2O was added and the mixture separated. The aqueous phase was washed with 100 mL ethyl ether. The combined organic phases were washed with 100 mL H_2O and then dried over Na_2SO_4. After concentrating the product solution on a rotary evaporator the products were distilled through a Ta wire column (isolated yield, 57%, >95% pure). The product was a colorless liquid but developed a pink color on short exposure to air at r.t; Bp 92-97° C (20 torr). ^{1}H-NMR ($CDCl_3$): δ0.09 (s,9H), 0.14 (s,9H), 0.88 (t,3H,J=7), 1.82-1.18 (m, 5H). IR (thin film): 2950, 2150, 1460, 1400, 1250, 1055, 960, 835, 760 cm^{-1}. HRMS: Calcd. for $C_{12}H_{26}Si_2$, 226.1573; found, 226.1578.

1,3-*Bis*(trimethylsilyl)pentyne: Prepared by the method described above for the hexynyl isomer. The product was a colorless liquid (bp 86-90° C, 30 torr) which rapidly turned pink on exposure to air at r.t. Isolated yield, 18g (62%) (>95% pure by VPC analysis). Preparative VPC gave samples of high purity for the following analyses: ^{1}H-NMR ($CDCl_3$): δ0.10 (s,9H), 0.16 (s,9H), 1.05 (t,3H,J=6), 1.23-1.68 (m,3H). IR (thin film): 2980, 2943, 2920, 2168, 1258, 1075, 1034, 990, 904, 850, 763, 702, 640, 618 cm^{-1}. HRMS: Calcd. for $C_{11}H_{24}Si_2$, 212.1416; found, 212.1419.

E- and Z-4-Ethynyl-5-(trimethylsilyl)ethynyl-4-octene: To an oven dried 100 mL round bottom flask capped with a rubber septum and flushed with N_2 was added 25 mL anhydrous ethyl ether and 1,3-<u>bis</u>(trimethylsilyl)hexyne (3.0 g, 13 mmol). With rapid magnetic stirring at -20° C, nBuLi (5.2 mL of a 2.4 M hexane solution, 13 mmol) was added over 10 min followed by TMEDA (1.5 g, 13 mmol). After stirring for 2 h the solution was cooled to -70° C and propyl ethynyl ketone (1.25 g, 13 mmol) was added in less than 3 sec (in order to minimize abstraction of the acetylenic hydrogen). The solution was slowly warmed to r.t. over 2 h and then stirred for an additional 1 h. The reaction solution was poured into 40 mL of an aqueous solution of NH_4Cl and then the organics were separated and washed 2 times with 40 mL H_2O. The organics were dried over Na_2SO_4 and then passed through 5 g silica gel to remove polymeric materials. Concentration on a rotary evaporator gave a light brown oil. Chromatography on 80 g silica gel using pet ether eluent gave satisfactory separation of the reaction products. Z-4-Ethynyl-5-(trimethylsilyl)ethynyl-4-octene: 0.61 g (22%) isolated yield, >98% pure (determined by VPC analysis). ^{1}H-NMR ($DCCl_3$): δ 0.16 (s,9H), 0.87 (t,6H,J=7), 1.43 (quintet,4H,J=7), 2.12 (t,4H,J=7), 3.13 (s,1H). IR (thin film): 3315, 3283, 2960, 2932, 2875, 2140, 1460, 1248, 870, 840, 756 cm^{-1}. <u>Anal.</u> Calcd. for $C_{15}H_{24}Si$: C, 77.54; H,10.41. Found: C, 77.72; H, 10.34. E-4-Ethynyl-5-(trimethylsilyl)ethynyl-4-octene: isolated yield, 0.50 g (15%). ^{1}H-NMR ($CDCl_3$): δ 0.16 (s,9H), 0.85 (t,6H,J=7), 1.46 (quintet,4H,J=7), 2.30 (t,4H,J=7), 3.30 (s,1H). IR (thin film): 3315, 2962, 2932, 2876, 2138, 1460, 1250, 1167, 964, 872, 840, 756 cm^{-1}. <u>Anal.</u> Two attempts were made to obtain an elemental analysis of this compound. The results were unsatisfactory due to decomposition of the sample during handling. HRMS: precise mass calcd. for $C_{15}H_{24}Si$, 232.1647; found, 232.1648.

E- and Z-hexa-1-trimethylsilyl-2,3-diethyl-1,5-diyn-3-ene: These compounds were prepared by the procedure described immediately above. Z-hexa-1-trimethylsilyl-2,3-diethyl-1,5-diyn-3-ene: Isolated yield, 1.23 g (17%). ^1H-NMR ($CDCl_3$): δ0.21 (s,9H), 1.07 (t,6H,J=7), 2.19 (quartet,4H,S=7), 3.12 (s,1H). IR (thin film): 3320, 3295, 2980, 2944, 2880, 2140, 1468, 1546, 1251, 1161, 1048, 984, 958, 905, 842, 759 cm^{-1}. HRMS: precise mass calcd. for $C_{13}H_{20}Si$, 204.1334; found, 204.1335. E-hexa-1-trimethylsilyl-2,3-diethyl-1,5-diyn-3-ene: Isolated yield, 0.6 g (9%). ^1H-NMR ($CDCl_3$): δ0.21 (s,9H), 1.07 (t,6H,J=6), 2.36 (quartet,4H,J=6), 3.32 (s,4H). IR (thin film): 3320, 2980, 2942, 2880, 2135, 1466, 1255, 987, 894, 850, 759 cm^{-1}. HRMS: precise mass calcd. for $C_{13}H_{20}Si$, 204.1334; found, 204.1335.

Z-4,5-Diethynyl-4-octene (19): This compound was prepared from Z-4-ethynyl-5-(trimethylsilyl)ethynyl-4-octene in 81% yield by the method of Arens and Schmidt.[26] The reaction products were passed through a short column of silica gel after workup and 0.41 g **19** was obtained >98% pure (determined by VPC analysis). Product **19** was a clear liquid which discolored rapidly upon standing at r.t. ^1H-NMR ($CDCl_3$): δ0.80 (t,6H,J=7), 1.42 (sextet,4H,J=7), 2.06 (t,4H,J=7), 3.05 (s,2H). IR (thin film): 3316, 3292, 2964, 2938, 2878, 2097, 1460, 1380, 1250, 1110, 1090, 842, 792, 736 cm^{-1}. Anal. The sensitivity of **19** to air and thermal decomposition resulted in an unsatisfactory elemental analysis. HRMS: precise mass calcd. for $C_{12}H_{16}$, 160.1252; found, 160.1253.

Z-Hexa-2,3-diethyl-1,5-diyn-3-ene (21): Prepared as for **19** above. ^{1}H-NMR ($CDCl_3$): δ 1.11 (t,6H,J=8), 2.22 (quartet,4H,J=8), 3.17 (s,2H). IR (thin film): 3292, 2980, 2943, 2882, 2097, 1466, 1380, 1250, 1055, 952, 887, 630 cm^{-1}. HRMS: precise mass calcd. for $C_{10}H_{12}$, 132.0939; found, 132.0939.

E-Dodeca-4,8-diyn-6-ene and E-deca-3,7-diyn-5-ene: The procedure reported by Ukhin and coworkers for the preparation of E-hexa-1,6-diphenyl-1,5-diyn-3-ene, except for the workup, was employed.[45] The workup was changed as follows: the reaction solution was cooled to r.t. and filtered to remove the copper salts. The solids were washed with petroleum ether and the combined organic solutions were washed twice with aqueous 10% HCl and once with H_2O. After drying over Na_2SO_4, the solution was concentrated on a rotary evaporator to produce a brown oil. The oil was chromatographed on silica gel using pet ether as eluent and the desired product was obtained in >95% purity. Both diacetylenes crystallized from pet ether solution at -20° C and could be further purified by drawing off the supernatant liquid with a pipet. E-dodeca-4,8-diyn-6-ene: isolated yield, 75%. ^{1}H-NMR ($CDCl_3$): δ 0.98 (t,6H,J=7), 1.54 (sextet,4H,J=7), 2.31 (t,4H,J=7), 5.87 (s, 2H). IR (thin film): 3035, 2962, 2936, 2875, 2817, 2220, 1753, 1460, 1428, 1380, 1338, 1327, 1278, 935 cm^{-1}. <u>Anal.</u> Calcd. for $C_{10}H_{12}$: C,89.93; H, 10.07. Found: C, 89.84; H,9.99. E-Deca-3,7-diyn-5-ene: isolated yield, 71%. ^{1}H-

NMR (CCl_4): δ1.13 (t,6H,J=8), 2.28 (quartet,4H,J=8), 5.70 (s,2H). IR (thin film): 3030, 2980, 2940, 2910, 2878, 2842, 2220, 1455, 1435, 1320, 1185, 1060, 938 cm^{-1}. HRMS: precise mass calcd. for $C_{10}H_{12}$, 132.0939; found, 132.0938.

Z-Dodeca-4,8-diyn-6-ene (23) and Z-deca-3,7-diyn-5-ene (24): Trans **23** and trans **24** were photoisomerized as follows: after deaeration, a solution of the diacetylene in pet ether (<2% v/v) was photolyzed in a quartz vessel with a medium pressure Hg lamp. The photolysis was monitored by VPC (Column A) and stopped when the photostationary ratio of the cis and trans isomers was reached (ca. 40:60). The mixture of geometric isomers was separated by column chromatography on silica gel (pentane eluent). The cis isomer was obtained in high purity (>95%). Compound **23**: ^1H-NMR ($CDCl_3$): δ1.04 (t,6H,J=7), 1.62 (sextet,4H,J=7), 2.41 (t,4H,J=7), 5.74 (s,2H). IR (thin film): 2960, 2930, 2870, 2210, 1675, 1575, 1461, 1452, 1427, 1392, 1378, 1334, 1324, 1274, 740 cm^{-1}. Anal. Calcd. for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 90.03; H, 9.99. Compound **24**: ^1H-NMR (CCl_4): δ1.19 (t,6H,J=7.5), 2.36 (quartet,4H,J=7.5), 5.57 (s,2H). IR (thin film): 3026, 2978, 2940, 2916, 2778, 2208, 1556, 1396, 1160, 1100, 1056, 740 cm^{-1}. HRMS: precise mass calcd. for $C_{10}H_{12}$, 132.0939; found 132.0938.

2,2,5,5-tetradeuterio-1,4-cyclohexadiene: 1,4-Cyclohexadiene-d_4 was prepared by base catalyzed exchange of the allylic protons for deuterium by treatment with d_5-dimsyl anion in DMSO-d_6: to oil free[46] NaH (24 mmol) was added dry DMSO-d_6 (Merck and Co., 99.5% D, 0.29 mol) in a flask fitted with a condenser (5° C) and flushed with N_2. The mixture was heated to 75° C for 45 min to generate the dimsyl anion.[46] The solution was cooled to 23° C and, with rapid stirring, 1,4-cyclohexadiene (43 mmol) was added as fast as possible. A red color rapidly developed and the reaction was quenched by addition of D_2O (50 mmol, 99.7% D) after 1 min. Hexadecane (15 mL) and ice water (30 mL) were added and, after stirring for several minutes, the mixture was forced through a coarse-frit filter to remove solids. The organic phase was removed and washed twice with cold H_2O. The aqueous phase was washed twice with hexadecane and the organic phases were combined and dried over Na_2SO_4. The volatiles were isolated by bulb to bulb distillation at 0.05 torr. Preparative VPC (Column A, 30° C) gave 21% isolated yield of 1,4-cyclohexadiene with 92% deuterium incorporation in the allylic positions. After additional drying over Na_2SO_4 the exchange was repeated a second time; the isolated yield after 2 exchanges was 9% and by ^{1}H-NMR and MS the product was observed to have 97.7% deuterium incorporation in the allylic positions. The primary complication encountered with this procedure was the presence of competing reactions which generated benzene and cyclohexene. Exchange was the (slightly) faster process; short reaction times minimized side product formation. Perhaps the best way to improve this reaction would be to use an additional solvent such as diglyme which may be cooled to lower temperatures lower than those obtainable using neat DMSO.

Thermal Reactions

Pyrolysis of Z-4,5-diethynyl-4-octene (19): The gas phase pyrolysis was performed under a flow of N_2 with a contact time of ca. 2 min and an oven temperature of 320° C. The pyrolysate, composed of **23**, **25** and **26**, was a yellow liquid at r.t. The isolated yield of products was 76%. Preparative VPC (Column B, 70° C) yielded the pure products. Thermal reactions of **19** in solution were analyzed on Column C using the following temperature program: initial temp. 150° C for 15 min; increase at 5° C/min; hold at 220° C for 20 min. The injector temperature was kept $<235^\circ$ C to prevent significant injector port reaction of **19**. Compound **28** was obtained pure for analysis from the thermal reaction of 5 mL of a 3×10^{-2} M solution of **19** in 1,4-cyclohexadiene plus chlorobenzene (10% v/v), followed by preparative VPC on Column A (at 125° C).

Benzocyclooctene (25):[29] ^{1}H-NMR (CCl_4): δ 1.34 (br m,4H), 1.66 (br m,4H), 2.67 (d of d,4H,J=5), 6.93 (s). IR (thin film): 3000, 2910, 2836, 1486, 1463, 1445, 1353, 1110, 748, 704 cm^{-1}. HRMS: precise mass calcd. for $C_{12}H_{16}$, 160.1252; found, 160.1258.

o-Allyl-n-propylbenzene (26): ^{1}H-NMR (CCl_4): δ 0.97 (t,3H,J=7), 1.60 (sextet,2H,J=7), 2.54 (T,2H,J=7), 3.32 (d,2H,J=7), 4.74-5.12 (m,2H), 5.65-6.18 (m,1H), 7.00 (s,4H). IR (CCl_4): 2940, 2915, 2855, 1635, 1435, 990, 915 cm^{-1}. HRMS: precise mass calcd. for $C_{12}H_{16}$, 160.1252; found 160.1250.

o-Dipropylbenzene (28): ^{1}H-NMR (CCl_4): δ 0.97 (t,6H,J=7), 1.60 (sextet,4H,J=7), 2.56 (t,4H,J=7), 6.98 (s,4H). IR (thin film): 3062, 3018, 2962, 2936, 2874, 1488, 1466, 1452, 1376, 746

cm^{-1}. HRMS: precise mass calcd. for $C_{12}H_{18}$, 162.1408; found, 162.1414.

Acid catalyzed exchange of aromatic hydrogen in 28:[31] A solution of **19** in chlorobenzene plus cyclohexadiene-d_4 (8.3% v/v) was heated at 190^{o} C for 15 min in a sealed glass tube. The solution was then concentrated to 0.3 mL total volume by static transfer (0.05 torr) of solvent. The solution was divided into two samples which were each treated in the following way: The chlorobenzene solution was placed in a glass tube with 0.5 mL of an aqueous solution of HCl (4% v/v). After freeze-pump-thawing to remove oxygen the tubes were sealed and heated at 260^{o} C for 42 h. The tubes were opened and the organic phases were removed by pipet. After VPC-MS analysis of **28** for deuterium content the solution was sealed in a tube as before with fresh aqueous HCl. After a second period of heating, VPC-MS analysis of **28** indicated no further change in the deuterium content (Scheme XIII).

Pyrolysis of Z-hexa-2,3-diethyl-1,5-diyn-3-ene (21): Gas phase and solution thermal reaction of **21** gave the products shown in Table 3. The solution and gas phase reaction mixtures were analyzed by VPC-MS. o-Ethylstyrene and tetralin were isolated from the gas phase reaction mixture by preparative VPC (Column A, 90^{o} C) and identified by comparison of their NMR spectra with authentic samples.[47] Benzocyclobutene and o-diethylbenzene were identified by VPC retention time (Column C, initial temperature = 105^{o} C for 15 min, temperature program = 6^{o}/min, final temperature = 200^{o}) and by comparison with the mass spectra obtained from authentic samples under identical conditions of analysis.

CIDNP experiment using Z-4,5-diethynyl-4-octene (19): Solutions of **19** (0.1-0.5M) in diphenyl ether and o-dibromobenzene gave identical CIDNP signals upon reaction in the heated probe of a Varian EM-390 ^{1}H NMR spectrometer (155-170^{o} C). At the concentrations employed, reduction to yield o-dipropylbenzene occurred to the extent of <u>ca</u>. 5% of the yield of the unimolecular products; otherwise, the product distributions were the same as that observed in more dilute solution pyrolyses.

Chapter III

DETERMINATION OF THE REACTIVE SPIN STATE OF 1,4-DEHYDROBENZENES

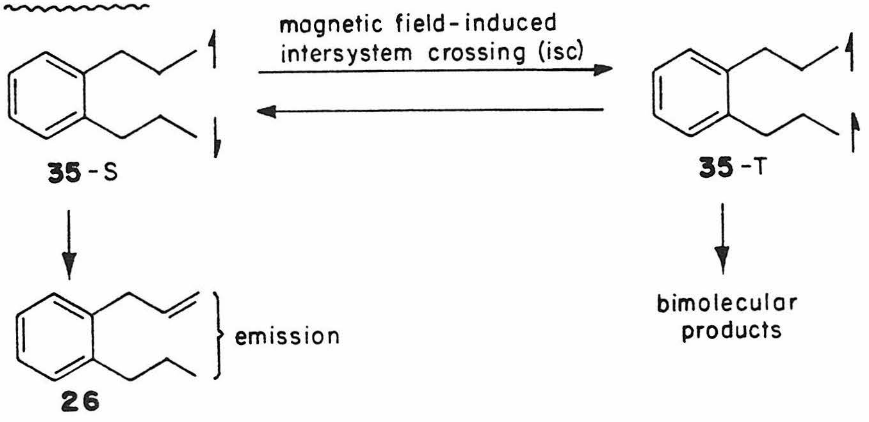
Introduction

In spite of the efforts of numerous investigators to generate and study the chemistry of 1,4-dehydrobenzene, the spin states populated under the reaction conditions have yet to be characterized. This is a particularly intriguing problem because the singlet and triplet states are presumed to be close in energy and because of the failure of theoretical treatments to reach a consensus in predicting the ground electronic state (Table 1, Chapter I). To date, the only reported experimental attempt to determine the spin state of a 1,4-dehydroaromatic is that of Chapman and coworkers[8], who generated 9,10-dehydroanthracene (**9**, Chapter I) in a matrix at 8° K and searched, without success, for an ESR signal which would have indicated population of the triplet state. In this chapter we detail our efforts to determine the number and description of the reactive spin states of the intermediates generated by the thermal reaction of diethynyl olefins in solution. Our approach includes both chemically induced dynamic nuclear polarization (CIDNP) and chemical trapping experiments.

As described in the preceding chapter, when **19** (cf. Scheme XII) was heated in a ^{1}H-NMR probe at 160° C, emissive signals were observed in **26** both in the vinyl protons and the terminal methyl and methylene protons of the alkyl side chain (figure 5). The location of the protons in **26** which showed emission indicates that biradical **35** is the molecule in which the CIDNP effects arose. The following observations are inconsistent with S-T_0 mixing and indicate instead an S-T_- mixing mechanism:[48] (1) The protons alpha and beta to the radical centers showed the same polarization; this indicates that the sign of the hyperfine interaction has no effect on the spectrum. (2) All of the polarized signals were emissive; normally, for polarizing radicals with a g-value difference of zero, a mixture of enhanced absorption and emission (multiplet effect) is observed. The S-T_- mechanism has been observed at high magnetic fields only in small biradicals (unpaired electrons separated by fewer than ca. 10 carbon atoms).[48,49]

Closs[48] has delineated two mechanisms by which the CIDNP effects observed in **26** may be explained: if singlet **35** is present and is higher in energy than triplet **35**, emissive signals may be observed if there exists a bimolecular reaction channel which drains off the triplet biradical formed by magnetic field-induced intersystem crossing (isc, Scheme XVI). On the other hand, if triplet **35** is produced in the reaction (by magnetic field-independent intersystem crossing in either **33**, **34** or **35**) and the ground state of biradical **35** is a triplet, then T_--S mixing can produce the observed signals, even in the absence of a spin-selective reaction channel. This analysis indicates that either singlet or triplet **35** may produce the observed polarizations; furthermore, it is difficult to distinguish between these possibilities on the basis of the experimental observations. If the triplet of **35** is produced in the reaction of **19**, three distinct modes of population of the triplet manifold are possible. Scheme XVII indicates that intersystem crossing in the 1,4-dehydrobenzene biradical, **34** or **35** could all have led to the formation of some fraction of **35** in the triplet state. Thus, even if triplet **35** is present it cannot be determined unambiguously in which of the three biradicals intersystem system crossing occurred.

Scheme XVI

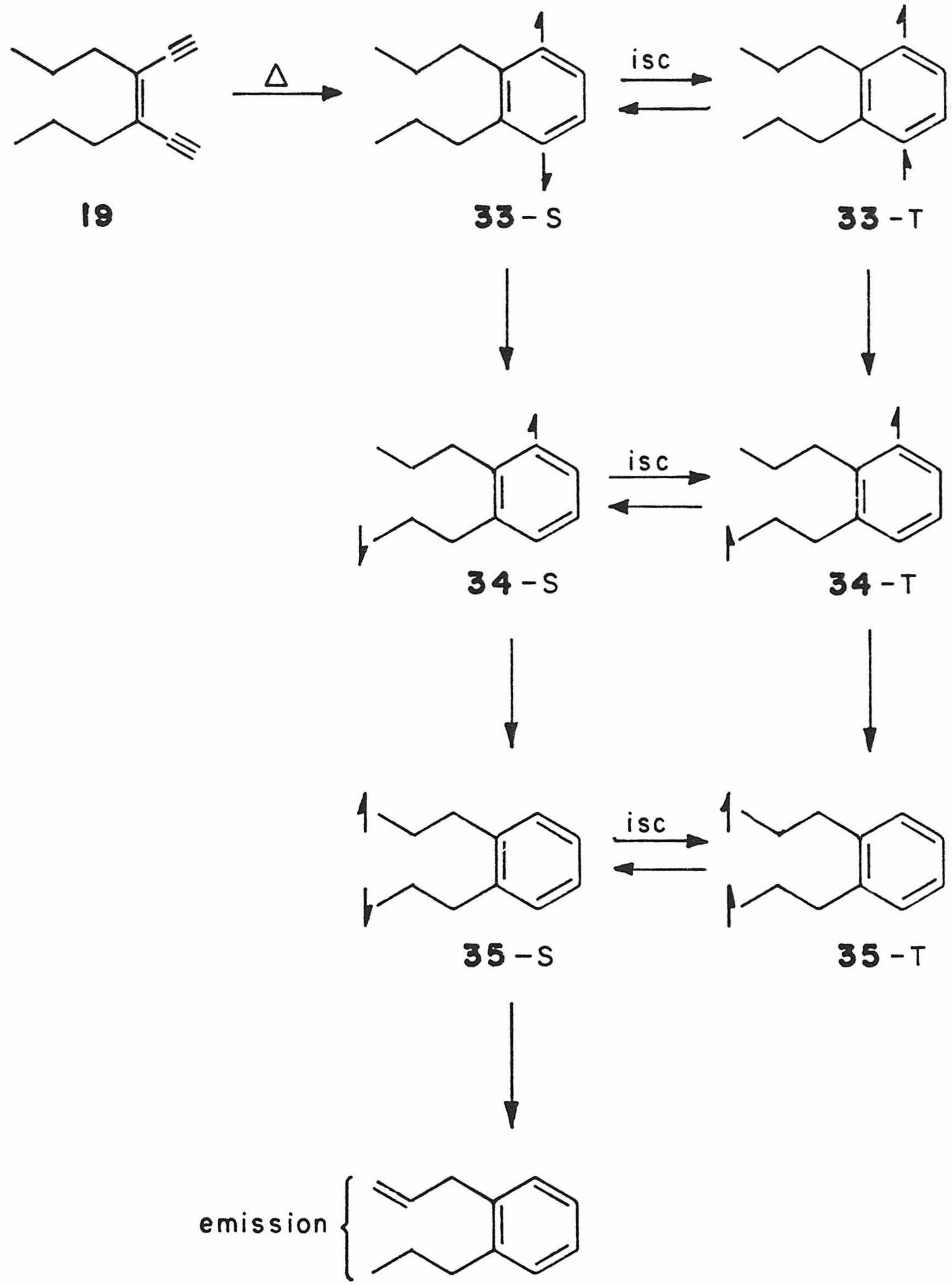


Results and Discussion

CIDNP

A more straightforward CIDNP analysis may be obtained by looking for polarization effects in the products of bimolecular reaction of the 1,4-dehydrobenzene biradical. This approach has been successfully applied in the thermal reaction of 2,3-dimethyl-hexa-1,5-diyn-3-ene (**38**). When a solution of **38** in hexachloroacetone (0.1 M) was heated to 160° C in the probe of a

Scheme XVII



90 MHz ^{1}H-NMR spectrometer, the spectrum obtained showed an emission in the aromatic region (figure 7). VPC analysis of the solution after reaction showed the formation of 1,4-dichloro-2,3-dimethylbenzene (**39**) and 1-chloro-2,3-dimethylbenzene (**40**) (relative yields, ca. 3:1). Only minor amounts of other products were detected bv VPC. The emission observed during thermal reaction of **38** is assigned to the aromatic protons of **39**. The broad proton absorption in the alkyl region (figure 7, spectrum (C)) is attributed to polymerization products formed as a result of the relatively high concentration of **38** in the NMR experiment.

Thermal reaction of dilute solutions of **38** (0.01 M) in hexachloroacetone and CCl_4 gave results (Table 5) similar to the NMR experiment. Product **39** was isolated from a CCl_4 solution reaction by preparative VPC and characterized by IR, ^{1}H-NMR and HRMS.

Table 5. Reaction of 38[a] in Solution at 190°C.

	Absolute Yield (%)	
Solvent	39	40
hexachloroacetone	17	5
CCl_4	20	5

[a] $[38] = 10^{-2}$ M

The mechanism shown in Scheme XVIII is proposed to explain the reaction of **38** in hexachloroacetone. By analogy to the thermal chemistry of **19**, cyclization of **38** gives the 2,3-

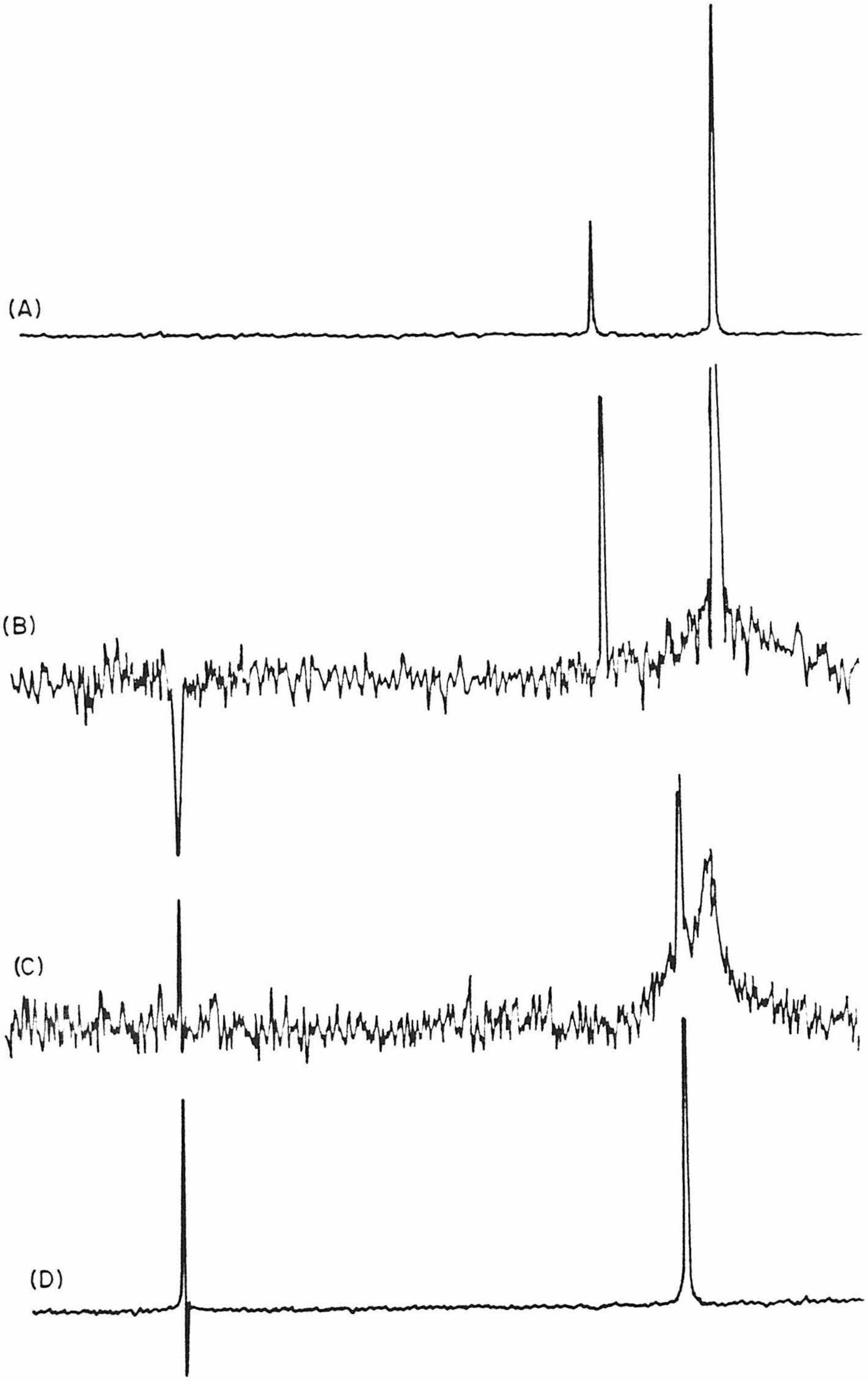


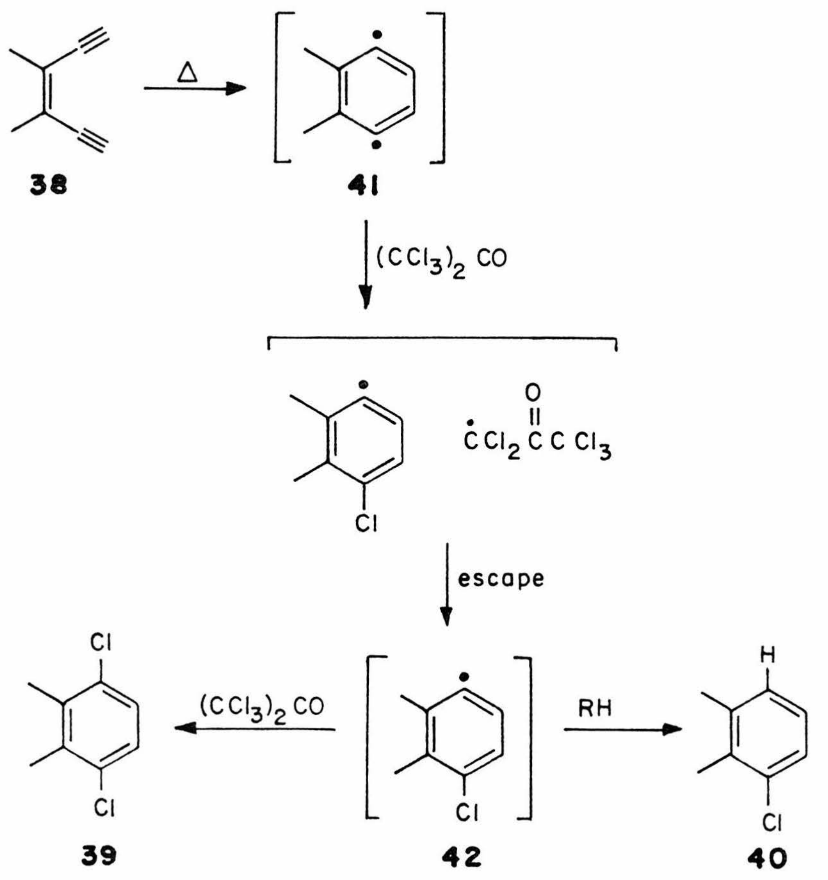
Figure 7. CIDNP observed during reaction of a hexachloroacetone solution of 38. (A) NMR of solution before reaction. (B) Signals observed during reaction at 160° C. (C) Room temperature spectrum after complete reaction of 38. (D) Spectrum of 39 in CCl_4.

dimethyl-1,4-dehydrobenzene biradical (**41**) which may abstract chlorine from solvent to produce a solvent-caged radical pair. Cage escape of the aryl radical (**42**) and abstraction of a second chlorine atom from the solvent gives **39**. Hydrogen abstraction reactions of **41** and **42** lead to **40**. The pentachloroacetonyl radicals generated by loss of chlorine may attack **38**; this is presumed to be responsible for the modest yield of aromatic products.

The observed polarizations can be readily interpreted by application of Kaptein's rules.[50] The analysis requires that (+) or (-) values be assigned to the parameters in equation 9. Because the aromatic signal appeared in emission, the product of the four parameters must be (-). Compound **39** was formed by escape from the polarizing pair, therefore ϵ is negative (-). The g value of **42** should be less than that of the pentachloroacetonyl radical (cf. g values of phenyl (2.0025) and dichloromethyl (2.0080))[51] so Δg = (-). The hyperfine coupling constant in phenyl radicals is positive for the ortho, meta and para hydrogens, so A_i = (+). The remaining parameter, μ, must be assigned a value which makes the product of the right hand side negative since the polarization in **39** was emissive; the sign of μ, therefore, is (-) which indicates that the spin state of the polarizing radical pair was a singlet. The singlet spin state of 1,4-dehydrobenzene **41** therefore must be the predominant source of product.

The CIDNP observed in **26** may be reinterpreted in light of the findings for **41** by postulating that the polarizations either

Scheme XVIII



$$\text{Kaptein's Rule:} \quad \Gamma_{\text{(observed polarization)}} = \mu \epsilon \Delta g A_i \qquad (9)$$

$$\Gamma \begin{cases} + = \text{absorption} \\ - = \text{emission} \end{cases}$$

$$\mu \begin{cases} + \text{ triplet radical pair} \\ - \text{ singlet radical pair} \end{cases}$$

$$\epsilon \begin{cases} + \text{ cage product} \\ - \text{ escape product} \end{cases}$$

$$\Delta g \begin{cases} + \\ - \end{cases} \text{sign of difference between g-factors}$$

$$A_i \begin{cases} + \\ - \end{cases} \text{sign of hyperfine coupling constant}$$

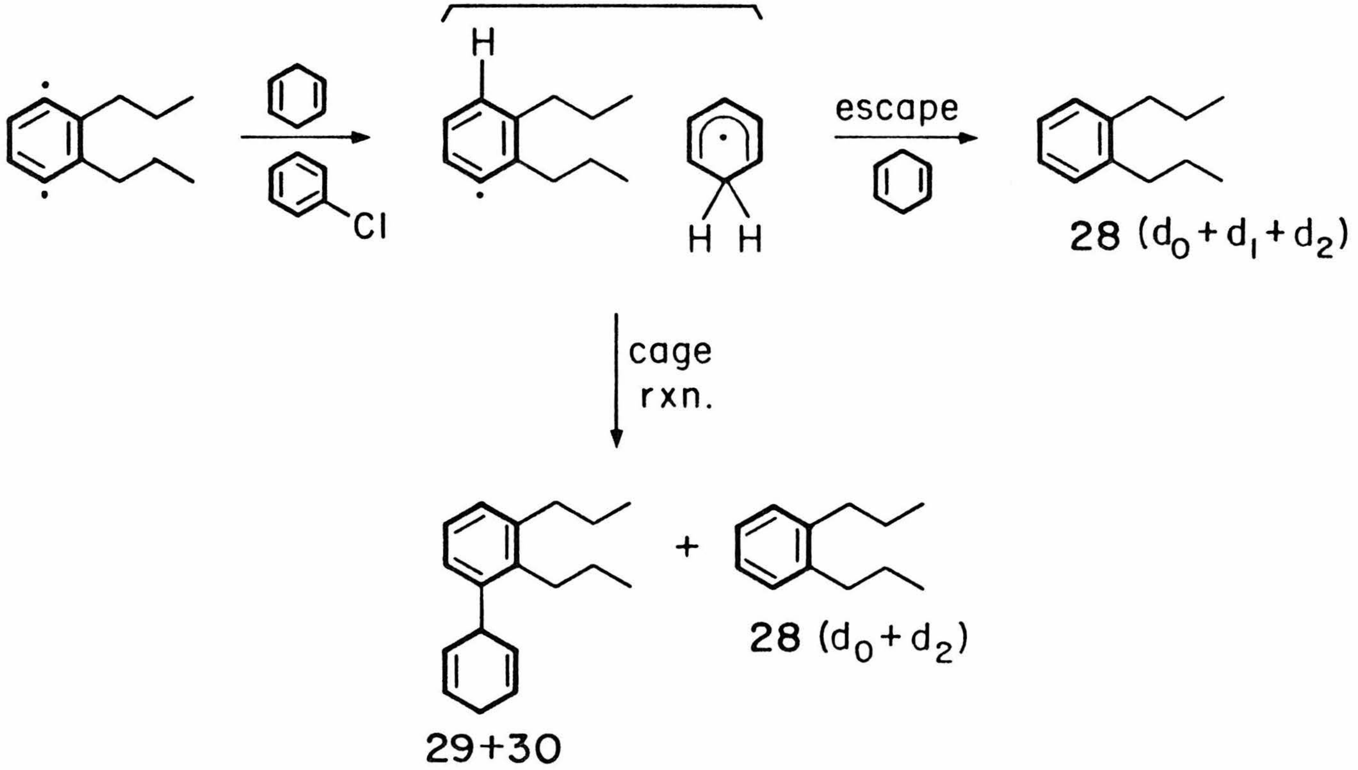
arose from singlet **35** or that triplet **35** was produced as a result of intersystem crossing in biradical **34** or **35** but not in the 1,4-dehydrobenzene biradical.

Chemical Trapping Studies

A second approach to determining the spin states present in solution involves an attempt to distinguish between the chemical reactivity of the triplet and singlet states of 1,4-dehydrobenzene **33**. Because radical pairs are generated by abstraction reactions of **33**, the task reduces to finding a way to differentiate the reactivity of singlet and triplet radical pairs.[52] The spin correlation effect (SCE)[53] postulates that radical pair reactivity is related to the spin state of the pair: singlet radical pairs may undergo both cage[54] and escape reactions but a spin prohibition against cage reactions limits triplet radical pairs to cage escape (in the absence of intersystem crossing).[55] In order to detect the presence of singlet and triplet radical pairs generated by trapping of singlet and triplet **33**, we must distinguish between the cage and escape pathways leading to product formation; the magnitude of the ratio of cage/escape reactions will reflect the spin state of the radical pair generated from **33**.

Scheme XIX illustrates the cage and escape reactions that can occur in the radical pair generated by hydrogen transfer from 1,4-cyclohexadiene to biradical **33**. While combination products **29** and **30** are unique to cage reaction,[56] **28** is produced both by

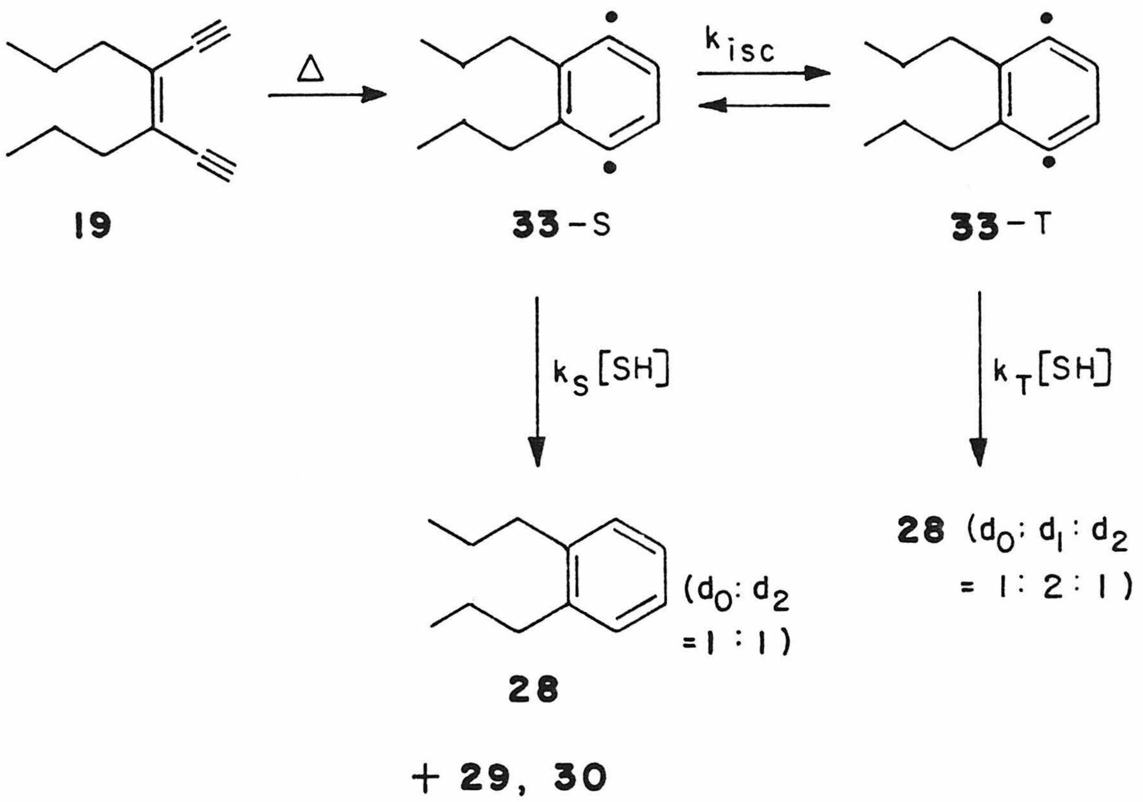
Scheme XIX



cage disproportionation and cage escape; it is necessary, therefore, to determine the extent to which the cage and escape reaction pathways contribute to the yield of **28**. It is possible to perform this analysis if a mixture of 1,4-cyclohexadiene-d_0 and -d_4 is used in the reaction solution. Consider first the reaction of **33** with cyclohexadiene-d_0. The cage reactions which the radical pair (formed by hydrogen transfer to **33**) may undergo include transfer of a second hydrogen atom to give **28**-d_0 and combination to produce products **29** and **30**. Escape of the aryl radical from the solvent cage, followed by abstraction of hydrogen or deuterium from trapping agent will give **28**-d_0 and -d_1 in the ratio 1:1 in the absence of a deuterium isotope effect. By a similar analysis, if **33** initially interacts with deuterated trapping agent, **28** formed by cage reaction will contain two deuteria while cage escape will lead to **28**-d_1 and -d_2 in the ratio 1:1. In summary, cage reaction will lead to only **28**-d_0 and -d_2 (1:1 ratio) and escape reactions of the radical pair should give **28**-d_0, -d_1 and -d_2 in the ratio 1:2:1. Because **28**-d_1 is unique to the cage escape reaction channel, it is possible to dissect the experimentally observed ratio of **28**-d_0, -d_1 and -d_2 (obtained by mass spectroscopic analysis) into the relative contributions of the cage and escape pathways; when the yield of **29** and **30** is added to the yield of **28** produced by cage reaction, the ratio of cage to escape products (C/E) is obtained.

It is impossible to predict, a priori, the relative amounts of cage and escape reaction for a given singlet radical pair (the SCE postulates that C/E for a triplet pair is zero). For this

Scheme XX



reason an experimentally observed ratio of C/E by itself will provide limited quantitative information about the relative amounts of singlet and triplet **33** present in solution. The analysis is broadened, however, by consideration of the kinetic relationships in Scheme XX. Conservation of spin (in the cyclization reaction) requires that biradical **33** is initially generated in the singlet state. The ratio of trapping of the singlet biradical to intersystem crossing to triplet **33** will depend on the concentration of trapping agent in solution.[57] At low concentrations of cyclohexadiene intersystem crossing should be at its maximum value whereas a high concentration of the trapping agent will increase $k_T[SH]$ and the amount of intersystem crossing observed should be at a minimum.

Compound **19** (0.01 M) was allowed to react at 195° C in a chlorobenzene solution which contained added cyclohexadiene (d_0:d_4 = 1:4) ranging in concentration from 0.01 to 10.6 M. The data obtained by combined VPC and VPC-MS analysis are plotted in figure 8. The ratio C/E (0.55) did not vary, within experimental error, over the range 0.2 to 1.6 M cyclohexadiene. The ratio of C/E was experimentally difficult to determine for the entire product spectrum (**28**, **29** and **30**) at low concentrations of cyclohexadiene;[58] the ratio of C/E for product **28**, however, may be readily determined by VPC-MS analysis alone. As the lower plot in figure 8 shows, the ratio of C/E for product **28** (0.20) was independent of cyclohexadiene concentration from 0.01 to 10.6 M. The relatively large, constant value of C/E for the complete

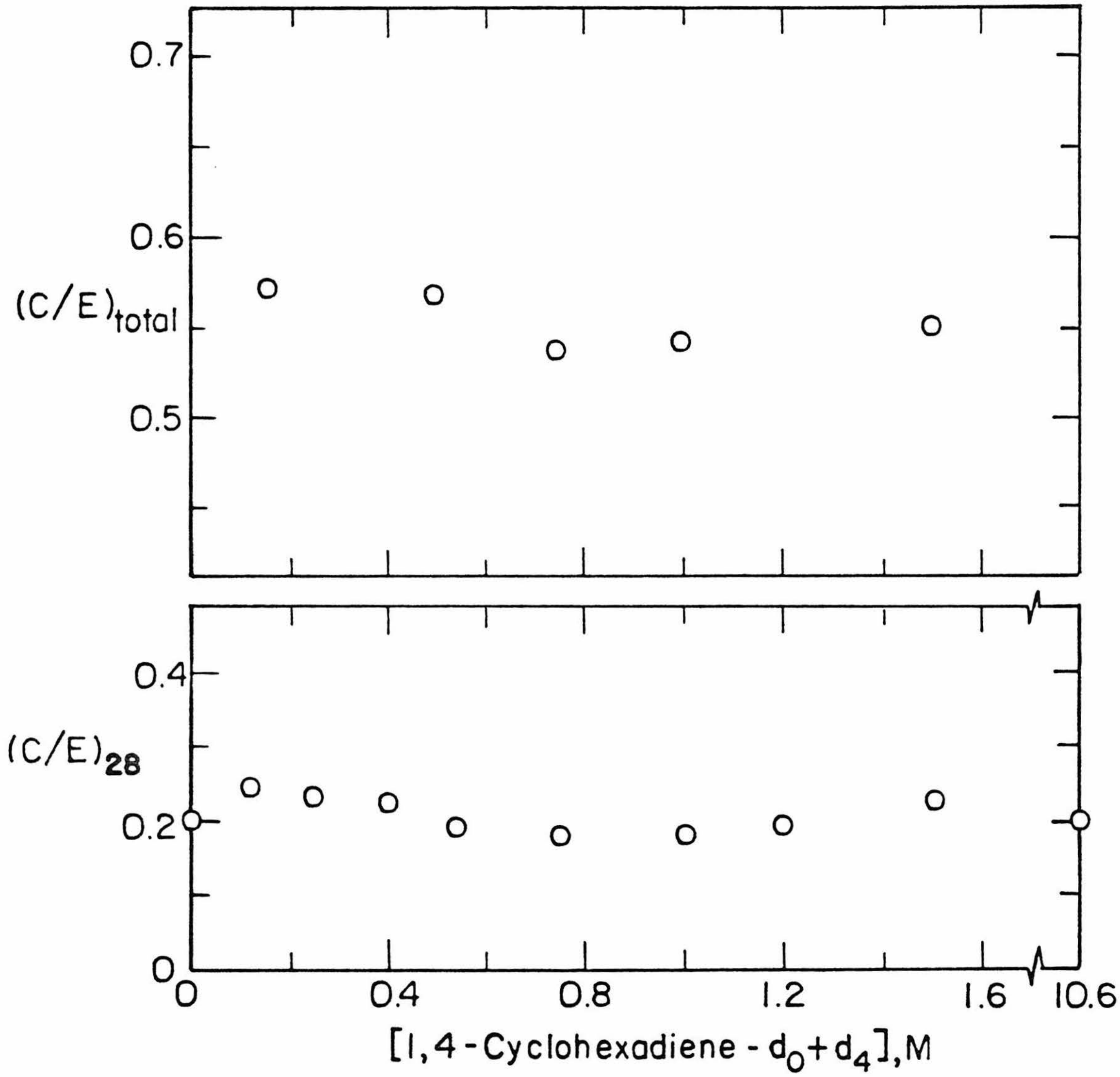


Figure 8. Ratio of C/E observed in the reaction of 19 (0.01 M, 195° C) as a function of 1,4-cyclohexadiene concentration. Upper plot shows C/E for products 28, 29 and 30. Lower plot shows C/E for product 28 alone.

product spectrum (ca. 0.55) indicates the presence of the singlet radical pair generated from the singlet state of **33**.

If the ground state of **33** is a triplet but intersystem crossing from the singlet is slow relative to unimolecular and bimolecular reaction, exclusive trapping of the singlet state will be observed at all concentrations of cyclohexadiene. One way to increase k_{isc} is to perform the reaction in a brominated solvent; the presence of bromine either in a reacting substrate or in the solvent is known from excited state chemistry to increase intersystem crossing rates (the heavy-atom effect).[59] When **19** was allowed to react in bromobenzene solution, the ratio of C/E was found again to be independent of cyclohexadiene concentration (figure 9). As before, the large value of C/E (ca. 0.64) suggests the exclusive formation of the singlet radical pair. The ratio C/E for product **28** (0.20) was also independent, within experimental error, of the concentration of cyclohexadiene.

As experiments described in Chapter II demonstrated, both **33** and **34** are trapped by 1,4-cyclohexadiene. In the spin state study described above two radical pairs were generated (from **33** and **34**) at low concentrations of cyclohexadiene and a single pair (from **33**) at high concentrations. However, because **34** is presumably produced from **33** without a change in spin multiplicity, the spin state analysis above may still be appropriate; this is strongly supported by the observation that the ratio C/E was independent of cyclohexadiene concentration even though the relative amounts of trapping of biradical **33** and

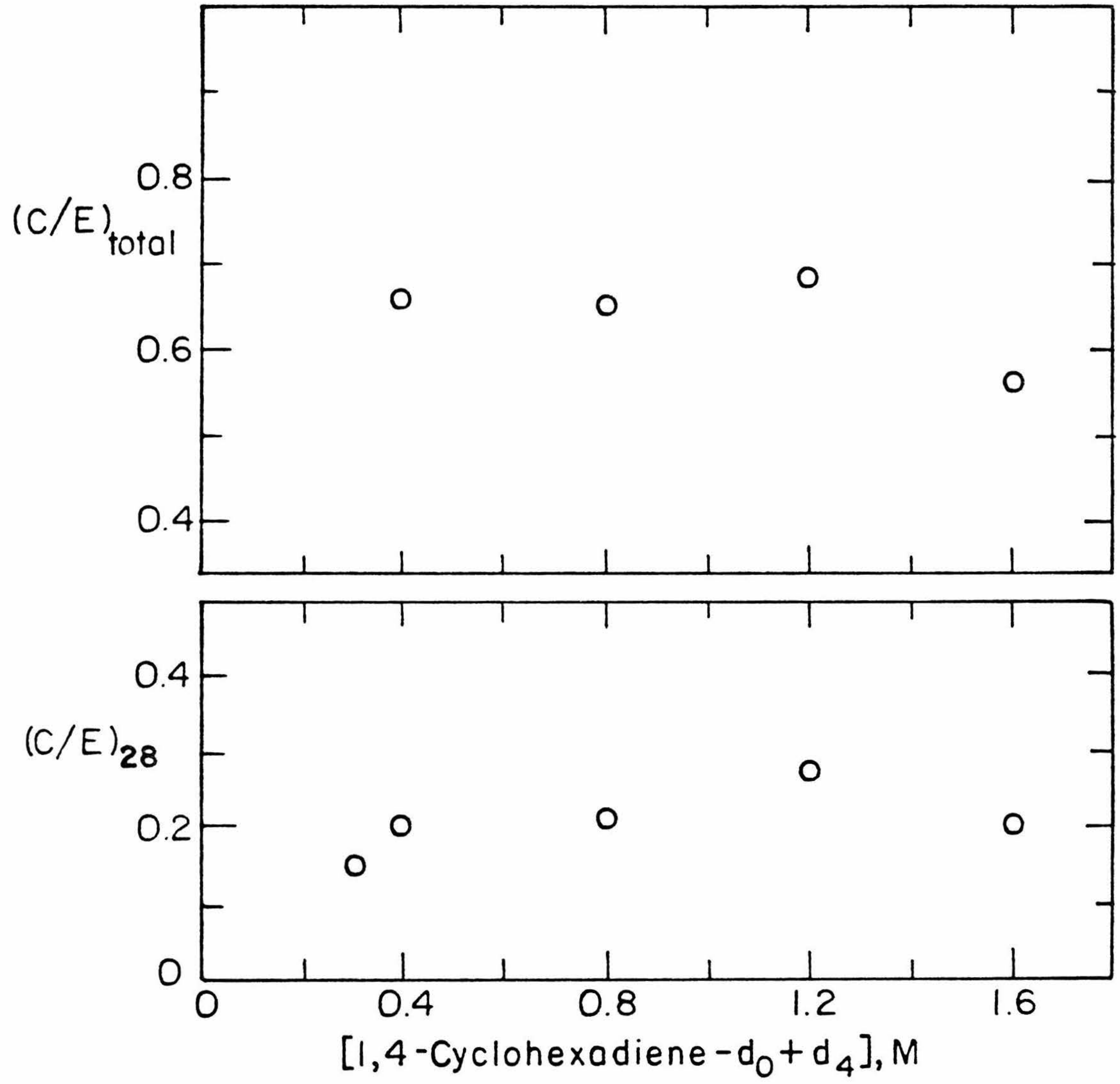


Figure 9. Ratio of C/E observed in the reaction of 19 (0.01M, 195° C) in bromobenzene solution as a function of added 1,4-cyclohexadiene. Upper plot shows C/E for products 28, 29, and 30. Lower plot shows C/E for product 28 alone.

34 varied considerably.

There are several alternatives to the conclusions drawn from the chemical trapping data. First, although the ratio C/E was found to have a value (ca. 0.6) which strongly suggests the presence of singlet **33**, the same value could have been obtained if extremely rapid intersystem crossing produced an equilibrium ratio of singlet and triplet **33** at all concentrations of cyclohexadiene. If this were the case, the ratio C/E would reflect a component of both the singlet (C/E > 0.6) and triplet (C/E ca. 0) radical pairs. Another way to explain the results is that k_{isc} and k_S[SH] are competitive, but k_T[SH] is very slow and failed to generate an appreciable amount of the triplet radical pair. It is difficult to imagine a factor that would lead to such an appreciable difference in the reactivity of singlet and triplet **33** toward cylohexadiene. A final possibility, which cannot be ruled out, is that k_{isc} is too slow to produce an observable amount of triplet **33** under the reaction conditions, even if the triplet state is equal to or lower in energy than the singlet. Unfortunately, the lifetime of 1,4-dehydrobenzene biradicals are limited by ring opening and other unimolecular reactions, even in the absence of bimolecular reaction channels. Generation of 1,4-dehydrobenzenes at lower temperature might favor intersystem crossing over other reaction pathways;[60] the rapid cyclization observed for cyclic diethynyl olefin **8** (Scheme V, Chapter I) at ambient temperature suggests one synthetic approach.

Conclusions

The unambiguous CIDNP result obtained in the reaction of **38** compares well with the chemical trapping study which indicates the presence of singlet state intermediates in the reaction of **19.** The failure to detect evidence for the population of triplet **33** or **41** in these studies may be due to the short lifetime of the 1,4-dehydrobenzene intermediates under the reaction conditions. A slow intersystem crossing rate will preclude observation of the triplet biradical even if it is the lowest energy state. The lifetime of 2,3-dialkyl substituted 1,4-dehydrobenzenes may be estimated from the parameters obtained for **33** in Chapter II; at 200° C, unimolecular ring opening occurs with a half-life of ca. 10^{-8} to 10^{-9} sec. Therefore, if the ground electronic state of 1,4-dehydrobenzenes **33** and **34** is the triplet, population from the singlet must occur with a rate constant $<10^{9}$ sec.

Experimental Section

General

See Chapter II for descriptions of NMR, IR and mass spectrometers, VPC chromatographs and columns used. The method of preparation of solution and CIDNP reaction samples has also been described.

Synthesis

2-Bromo-3-butyne: A procedure for a similar reaction has been outlined by Ashworth, Whitham and Whiting.[61] A dry ether solution (18 mL) of 1-butyn-3-ol (22.2 g, 0.317 mol) and pyridine (0.22 mL) were placed in a 3-neck flask fitted with an addition funnel, an argon inlet and a reflux condenser. To the argon-flushed flask cooled to 5° C was added an ether solution (12 mL) of freshly distilled PBr_3 (42.5 g, 0.317 mol) over 4 h. Reaction was complete at the end of the addition (VPC analysis on Column A, 45° C). Water was carefully added to the clear orange-brown reaction solution until fuming ceased. The organic phase was separated and washed with 50 mL of an aqueous $NaHCO_3$ solution followed by a wash with 50 mL brine. The ether solution was dried over $MgSO_4$; distillation through a Ta wire column at 1 atm gave 13.6 g (32% yield) of 2-bromo-3-butyne (>98% pure, as determined by VPC) bp 83-90° C. ^{1}H-NMR (CCl_4): δ 1.90 (d,3H,J=7), 2.53 (d,1H,J=2.5), 4.51 (d of q,1H,J=7,2.5). IR (thin film): 3300, 2950, 2120, 1430, 1370, 1300, 1180, 1090, 1060, 990, 970, 855 cm^{-1}. <u>Anal.</u> Calcd. for C_4H_5Br: C, 36.13; H, 3.75. Found: C, 35.95, H, 3.76.

3,4-Dimethyl-hexan-1,5-diyn-3-ol: An oven dried 3-neck flask was fitted with an addition funnel, condenser, thermometer and an argon inlet. Magnesium turnings (2.45 g, 0.10 mol) dry ethyl ether (10 mL) and a small amount of $HgCl_2$ were added. After the solution became cloudy the reaction flask was cooled to 10° C and an ethyl ether (65 mL) solution of 2-bromo-3-butyne (13.6 g, 0.10 mol) was added over 1.5 h. A clear, faint yellow solution resulted. The solution was cooled to -15° C and methyl ethynyl ketone (6.9 g, 0.10 mol) dissolved in ethyl ether (70 mL) was added over 1 h. A white ppt. formed after the addition was one-half complete. After the addition, the solution was warmed to room temperature over 0.5 h and poured into a cold, saturated aqueous NH_4Cl solution. The organics were isolated and the aqueous phase was washed three times with ethyl ether. The combined ethyl ether solutions were washed with 150 mL brine and then dried over Na_2SO_4. Concentration on a rotary evaporator gave a somewhat volatile reddish oil. The crude product was purified by passing through a pad of silica gel with a mixture of pet ether and ethyl ether as eluent (7:3 v/v). Static vacuum distillation (0.03 torr) of the oil gave 8.4 g (>98% pure as determined by VPC) of 3,4-dimethyl-hexan-1,5-diyn-3-ol (70%) as a colorless oil. The alcohol was formed as a mixture of diastereomers (5:1 ratio) which could be separated by preparative VPC (column B, 100° C). NMR of major diastereomer ($CDCl_3$): 1.33 (d,3H,J=7.5), 1.54 (s,3H), 2.19 (d,1H,J=2.5), 2.46

(s,2H,OH,acetylenic H), 2.65 (m,1H,J=7.5,2.5). IR (thin film): 3250, 3220, 2980, 2110, 1710, 1440, 1370, 1250, 1090, 1030, 1000, 970, 720 cm^{-1}. Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 82.5. Found: C, 78.36; H, 8.23.

2,3-Dimethyl-hexa-1,5-diyn-3-ene (38): A 25 mL 3-neck flask was fitted with an argon inlet, addition funnel and a stopcock through which aliquots could be removed. After flushing with argon, 3,4-dimethyl-hexan-1,5-diyn-3-ol (1.65 g, 0.011 mol) and pyridine (3.5 mL) were added. The mixture was cooled to 5^{o} C and a solution of $POCl_3$ (1.98 g, 1.2 mL, 0.013 mol) in pyridine (1.7 mL) was added with stirring over 30 min. The reaction was monitored by VPC (Column B, 98^{o} C). After the addition of $POCl_3$, little reaction had occurred, so the mixture was warmed slowly to r.t. After 1 h at room temperature the reaction was complete. The dark reaction mixture was poured over ice with pet ether and H_2O rinses. The organic layer was separated and the aqueous phase was washed 3 times with pet ether. The combined organics were washed with 10% aqueous HCl until acidic by litmus and then washed with H_2O to pH 4. The pet ether solution was dried over Na_2SO_4 and concentrated to give 0.63 g (50% yield) of an orange oil (>95% pure by VPC). Crystallization of cis and trans 2,3-dimethyl-hexa-1,5-diyn-3-ene (ratio 1:3) at -70^{o} C gave further purified product. The geometric isomers were isolated by column chromatography on silica gel (pet ether eluent). Cis isomer: NMR ($CDCl_3$): δ1.88 (s,6H), 3.17 (s,2H). IR (thin film): 3310, 3020, 2935, 2874, 2108, 1445, 1386, 1250, 1156, 1103 cm^{-1}. Trans isomer: NMR ($CDCl_3$): δ2.02 (s,6H), 3.36 (s,2H). IR (thin film): 3318, 2970, 2940, 2872, 2002, 1735, 1445, 1378, 1265, 1235, 1166, 1098, 800 cm^{-1}. HRMS: precise mass calcd. for C_8H_8, 104.0625; found for <u>cis</u> **38**, 104.0623; found for <u>trans</u> **38**, 104.0622.

<u>Thermal</u> <u>Reactions</u>

Reaction of 2,3-dimethyl-hexa-1,5-diyn-3-ene (38) in chlorinated solvents: CCl_4 (MCB spectral quality) was used without additional purification. Hexachloroacetone was purified by repeated distillation at 50 torr through a vacuum-jacketed glass helices-packed column. **38** was purified by preparative VPC (Column A, 85° C). n-Octane was used as an internal standard in the thermal reactions. Yields of products were determined by reference to the internal standard with the assumption that the response factor of the starting material and products were the same.[41] Pyrolyzed solutions were dark, guinness-brown, suggesting the occurrence of substantial polymerization. Reaction product **39** was isolated from the CCl_4 reaction mixture by preparative VPC (Column A, 135° C) and identified by NMR, IR and HRMS (see below). **40** was identified by its mass spectrum (m/e 140). No evidence for high molecular weight products, formed by combination of the radical pairs generated by transfer of chlorine (<u>eg</u>. Scheme XVIII), was detected by VPC-MS analysis of the hexachloroacetone solution reaction. In the CCl_4 reaction a product with m/e 256, 258, 260, 262 was detected; this may have been formed by the reaction of aryl radical **42** with the trichloromethyl radical. 1,4-dichloro-2,3-dimethyl-benzene (**39**): NMR (CCl_4): δ 2.33 (s,6H), 6.98 (s,2H). IR (CCl_4): 3020, 2940, 1875, 1458, 1413, 1389, 1264, 1161, 1136, 1030, 833, 590 cm^{-1}. HMRS: precise mass calcd. for $C_8H_8Cl_2$, 174.0003; found, 174.9999.

Reaction of 4,5-diethynyl-oct-4-ene (19) in cyclohexadiene-d_o and -d_4: Compound **19** was isolated >99% pure by preparative VPC and promptly dissolved in chlorobenzene to give a solution 0.01M in **19.** n-Undecane was added as an internal standard and the initial concentration of **19** was determined by comparison of the integrated analytical VPC peak areas. Cyclohexadiene-d_o and -d_4 were added to the chlorobenzene solution of **19** in a pyrolysis tube which was promptly sealed. After reaction for 15 min at 195° C, the solutions were very light yellow colored. The reacted solutions were analyzed by VPC (Column C, initial temp. 150° C for 15 min; increase at 5° C/min; hold at 220° C for 20 min) and the product yields determined by reference to the internal standard. The relative yields of **28**-d_o, -d_1 and -d_2 were determined by VPC-MS analysis (WCOT capillary column (see Experimental Section, Chapter II) initial temp. 110° C; increase at 4° C/min; hold at 220° C). The ratio of cyclohexadiene-d_o and -d_4 used was 1:4. With this ratio, **28**-d_o and -d_2 were formed in nearly equal yield (k_H/k_D is 4). The ratio of C/E was determined as follows: cage escape (E) is the only source of **28**-d_1; escape gives **28**-d_o, -d_1 and -d_2 in the ratio 1:2:1. Therefore, the escape component of **28**-d_o and -d_2 is 1/2 the yield of **28**-d_1. The remainder of **28**-d_o and -d_2 was formed by cage reaction (C) and was added to the yield of **29** and **30** to give the yield of cage products.

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54. The term "cage reaction" as applied in this discussion is meant to denote bimolecular reactions which take place within the geminate radical pair, ie., combination and disproportionation.

55. Since the lifetime of solvent-caged radical pairs is ca. 10^{-10} and the rate of intersystem crossing is ca. 10^{8} sec^{-1},[37] triplet-singlet interconversion should have an insignificant effect on the product distibution.

56. That **29** and **30** are formed solely by cage combination is demonstrated by the observation that, when **19** was allowed to react in the presence of cyclohexadiene-d_0 and -d_4, **29** and **30** contained only 0, 1 and 2 deuteria/molecule. Random combination of the aryl and cylohexadienyl radicals would have led to appreciable formation of the d_1 and d_3 isomers.

57. The ratio of cyclohexadiene-d_0 and -d_4 was held constant but the total concentration of trapping agent was varied.

58. At low concentrations of trapping agent, the yield of **28**, **29** and **30** was very small. Because **28** overlaps slightly with unimolecular product **26** in the VPC trace, small amounts of **28** were difficult to accurately measure. Likewise, because they refer to several isomeric, long retention time products, VPC integration of **29** and **30** was not accurate when low yields were produced in the reaction.

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Proposition Abstracts

Generation of Free and Metal-Bound Oxirenes. A synthetic route to oxirenes via 1-halo-2-trimethylsilylepoxides is proposed. Experimental methods which could be employed to establish the presence of oxirenes are described. A synthetic route to metal-bound oxirenes is also discussed.

Selective Pyrolysis by Multiphoton Infrared Excitation (MIRE). The use of tunable pulsed IR lasers as a heat source capable of inducing thermal reaction of selected components of a reaction mixture is proposed. Two specific examples where the method may be applied to unique advantage are described. In addition, a design for a preparative IR laser photolysis cell is suggested.

CIDNP as a Tool for the Study of the Photochemistry of Organosilicon Compounds. CIDNP holds great promise as a technique which may elucidate the details of silyl-radical generating photochemical reactions. To demonstrate the power of the method, the application of CIDNP to the study of four different photochemical reactions is discussed.

Investigations in Organometallic Photochemistry. An examination of the photochemistry of five metallocyclopentanes is proposed; these compounds have been selected because their structures may lead to unusual photochemical reactivity.

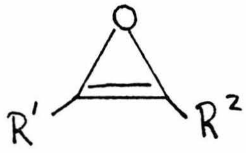
A Novel Synthetic Route to Binuclear Organometallic Compounds Containing a Bridging Methylene Function. A novel, and potentially general, method for preparing bridging methylene binuclear organometallic compounds is outlined.

GENERATION OF FREE AND METAL-BOUND OXIRENES

Introduction

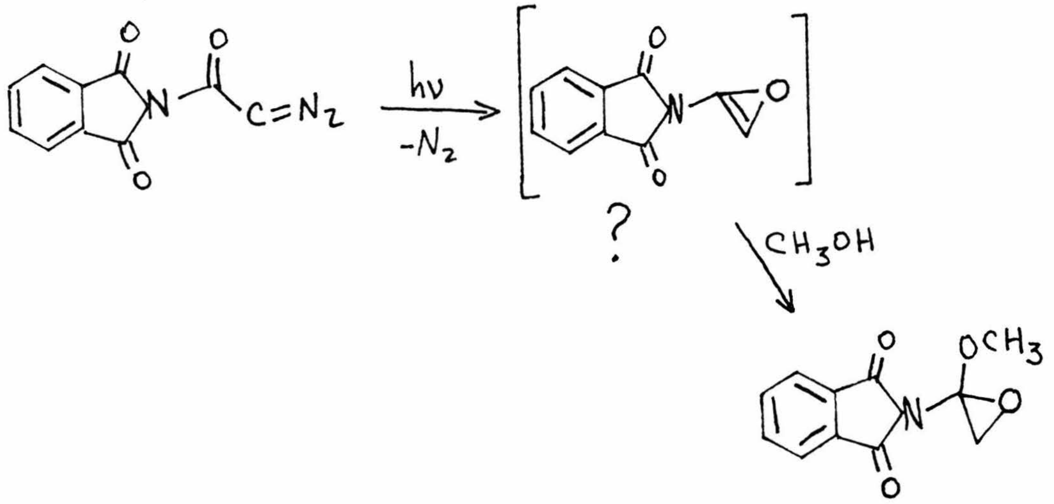
Oxirenes (**1**) have been invoked as intermediates in a number of reactions. Their formation in the reaction of alkynes with peracids[1] and in the reaction of methylene with carbon monoxide[2] has been proposed. Convincing evidence for the existence of oxirenes as intermediates (or transition states) comes from labelling results observed in the Wolff rearrangement of α-diazo ketones[3] (**2**, Scheme I). Nevertheless, to date there has been only a single, unpublished study in which a molecule containing the oxirene moiety appears to have been trapped (Scheme II).[4] Other efforts to trap or isolate oxirenes have been unsuccessful.[4,5]

Oxirene also has been of interest to theoretical chemists. Dewar and Ramsden[6] studied the rearrangement of formylmethylene (**3**, R^1,R^2 = H) to oxirene using MINDO/3 and NDDO semi-empirical methods. The results of their calculations led them to predict that oxirene is 18 to 20 kcal/mole more stable than formylmethylene. They also examined the energetics of motion along the energy surface and predicted an activation energy for the rearrangement of **1** to **3** of about 20 kcal/mole. An <u>ab initio</u> (LCAO-MO-SCF) calculation by Hopkinson[7] indicated **1** to be essentially isoenergetic with formylmethylene. In this calculation geometry was fixed at assumed parameters and no prediction was made concerning the energy surface connecting **3** and **1**. A more extensive <u>ab initio</u> (SCF-MO) study of the

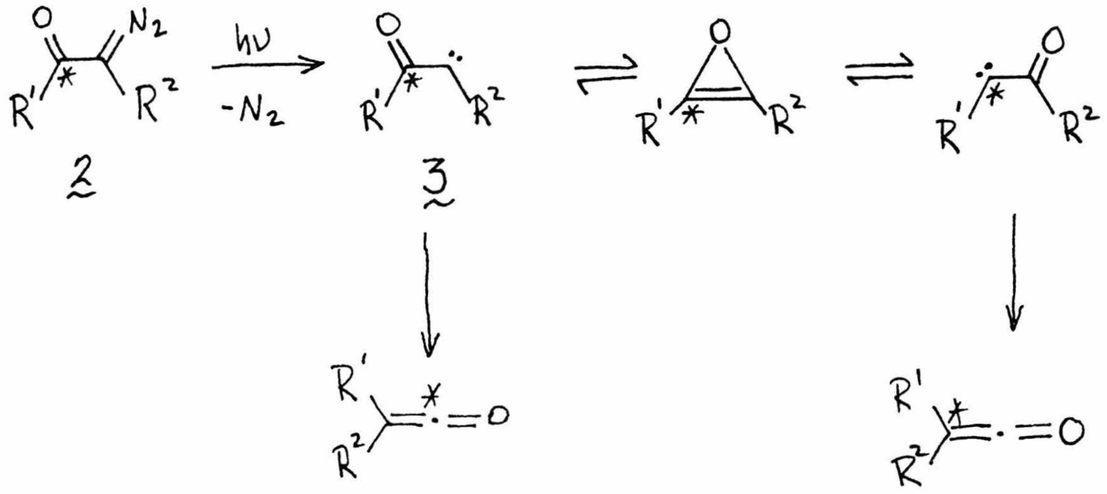


1

Scheme I



Scheme II



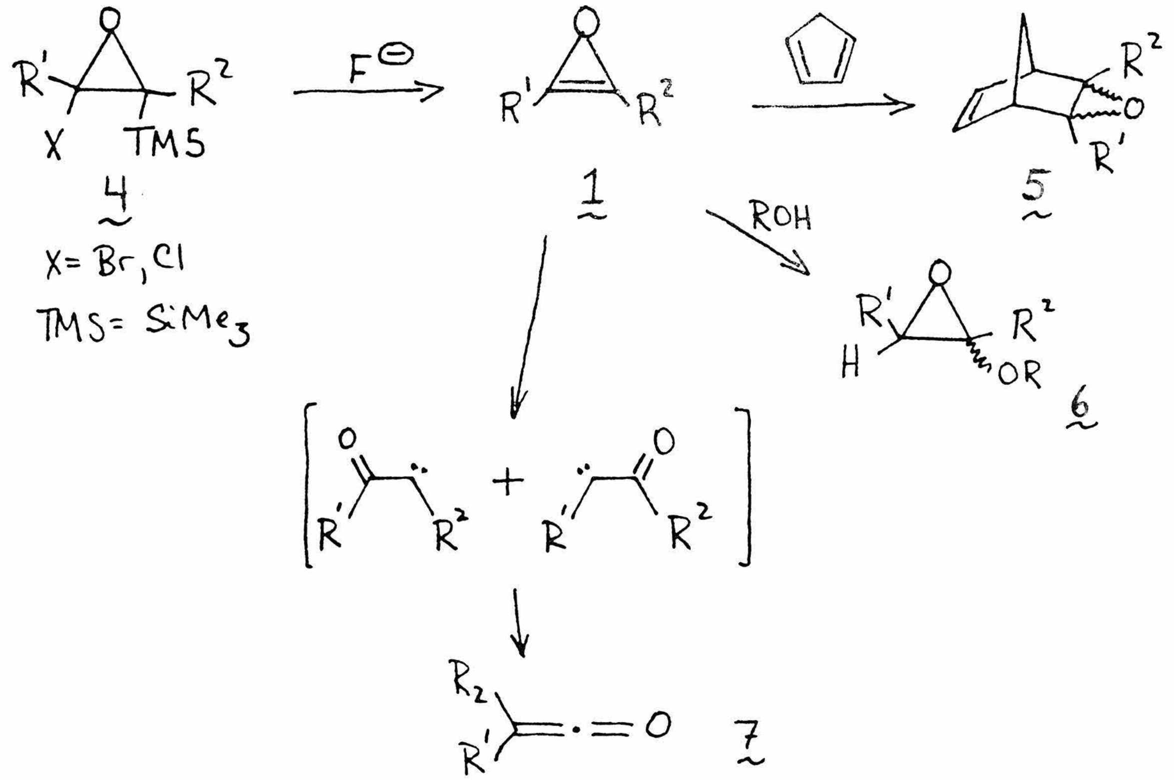
rearrangement was performed by Strausz and coworkers[8] and geometry optimization was carried out. Oxirene was predicted to be 12 ± 5 kcal/mole less stable than formylmethylene and the activation energy for the rearrangement of oxirene to formylmethylene was calculated to be 7 kcal/mole.[9] From these results it was predicted that oxirene has a lifetime of about 10^{-8} seconds at room temperature. In contrast to Dewar's studies, Strausz' result suggests that trapping of oxirene in solution will be possible only with high concentrations of a reactive trapping agent.

Proposal

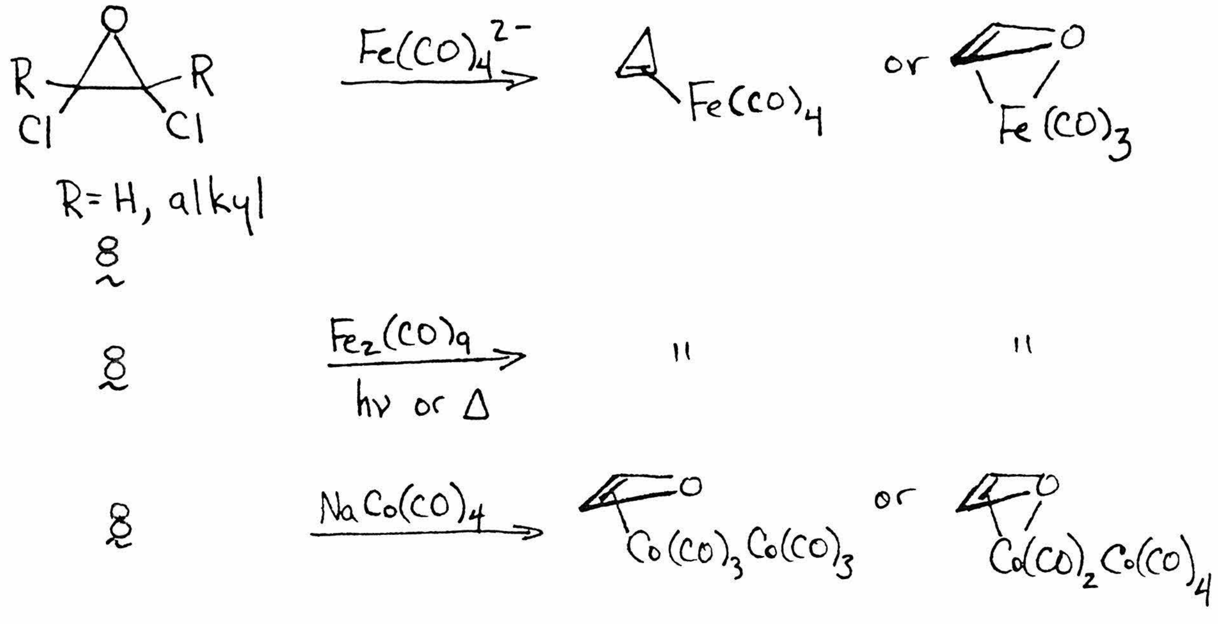
Generation of free oxiranes

A novel and effective route to oxirenes (**1**) may be possible by treating 1-halo-2-trimethylsilylepoxides (**4**) with cesium fluoride or tetraalkylammonium fluorides (R_4NF) in solution at, or somewhat below, room temperature (Scheme III). If oxirenes are successfully generated by this reaction, ring opening to α-keto carbenes followed by Wolff rearrangement to ketenes (**7**) should be observed.[3] The presence of a substantial concentration of cyclopentadiene or 1,3-diphenylisobenzofuran in the reaction solution may produce Diels-Alder trapping products (eg., **5**). Alternatively, it may be possible to trap the oxirene by performing the reaction in a solvent, such as an alcohol, with which it may rapidly react.[4] A kinetic analysis of the dependence of unimolecular reaction products (or products derived

Scheme III



Scheme IV



from **7** on the concentration of trapping agent may allow further demonstration of the intermediacy of **1** in these reactions.

If **1** is sufficiently long-lived, it may be possible to isolate the oxirene. A nitrogen gas purge of the reaction solution might liberate the oxirene which could be trapped in a low temperature matrix. Clearly, it will be possible to isolate **1** by this method only if the energy barrier separating the oxirene and α-keto carbene is larger than that predicted by Strausz and coworkers.

Preparation of Metal-Bound Oxirenes

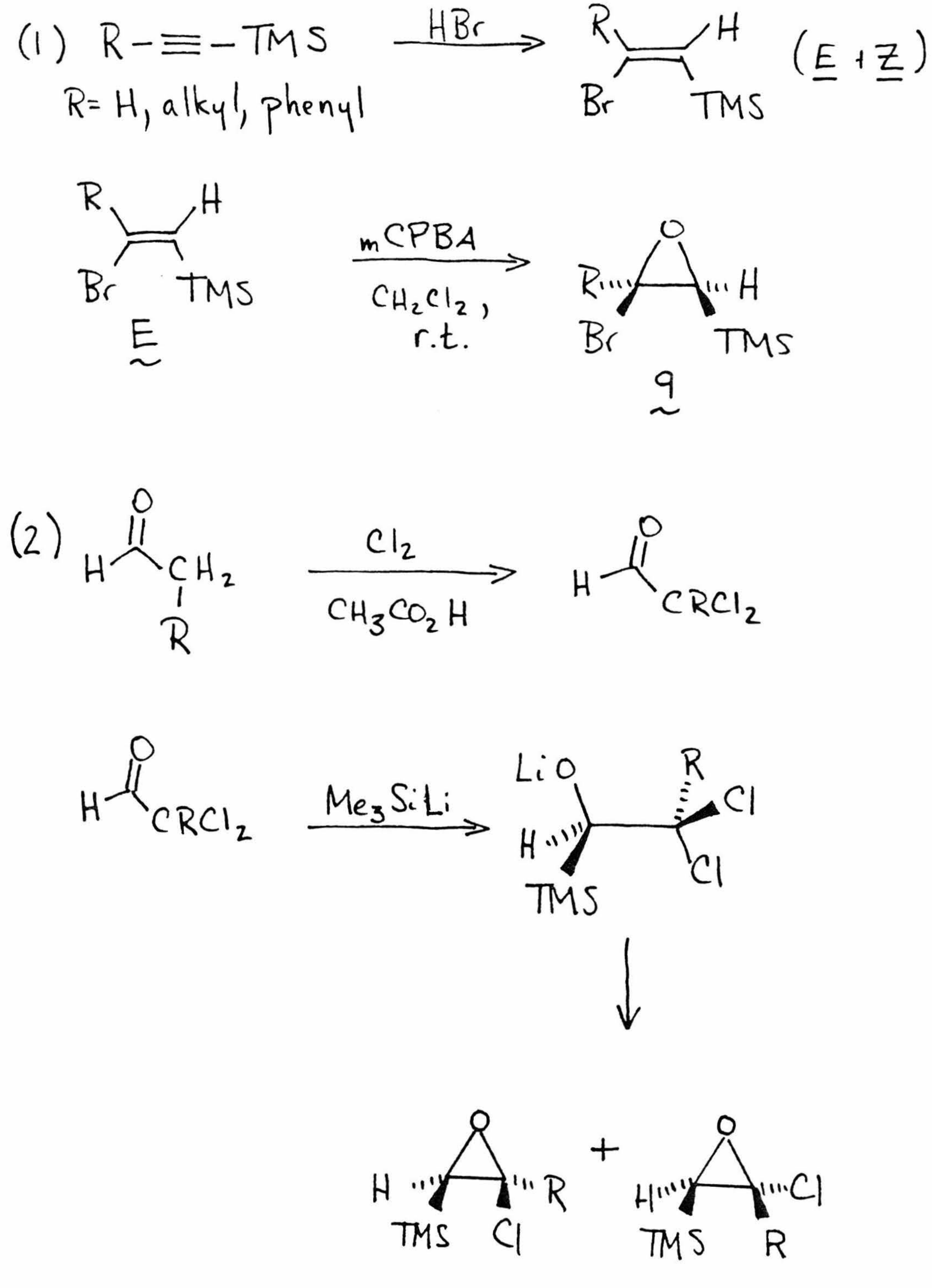
Metal coordination has been employed to stabilize several highly reactive organic molecules which otherwise have only transient existence at ambient temperature (cyclobutadiene[11] and trimethylenemethane[12] have both been isolated as metal-coordinated ligands). By a similar approach it may be possible to produce isolable metal-bound oxirenes. A synthetic route via 1,2-dichloro epoxides, which may be prepared by mCPBA epoxidation of 1,2-dichloro olefins, is possible.[13] Reaction of the 1,2-dichloro epoxides with a metal dianion such as Collman's reagent[14] (tetracarbonyl ferrate) may lead to displacement of both chlorines, with the generation of the metal-complexed oxirene (Scheme IV). Alternatively, reaction with $Fe_2(CO)_9$[11a] or $NaCo(CO)_4$,[11b] which have been employed to produce cyclobutadiene complexes from 3,4-dichlorocyclobutene, may produce coordinated oxirenes (Scheme IV). Behavior of the complexed ligand as a 2 or 4 electron donor could provide information on the amount of electron delocalization in the oxirene moiety.

Synthetic route to 1-chloro-2-trimethylsilylepoxides

Alkene synthesis via β-halo organosilicon compounds has been reviewed by Chan.[15] This exceptionally mild method has been used to generate several unstable olefins including allene oxides[16], strained bicycloalkenes[17] and anti-Bredt olefins.[18] The usefulness of this synthetic method for the preparation of high energy molecules is derived from the strength of the silicon fluorine bond, which is about 129 kcal/mole.

Two synthetic routes to 1-halo-2-trimethylsilylepoxides are proposed in Scheme V. A procedure for the hydrobromination of trimethylsilylpentyne has been described and should be readily adaptable to the preparation of various E- and Z-1-bromo-2-trimethylsilyl olefins.[19] Separation of the olefins followed by epoxidation with m-chloroperbenzoic acid (mCPBA)[20] should yield the respective syn and anti epoxides **9**. A second route to **9** involves the dichlorination of acetaldehydes in acidic medium.[21] Addition of trimethylsilyl lithium is expected to produce a mixture of the E and Z epoxides. Both methods may allow preparation of the bromo and chloro trimethylsilyl epoxides.

Scheme V


(1)
R−≡−TMS
R= H, alkyl, phenyl
HBr
R
H
Br
TMS
(E + Z)
R
H
Br
TMS
E
mCPBA
CH2Cl2, r.t.
O
R
H
Br
TMS
9
(2)
O
H
CH2
R
Cl2
CH3CO2H
O
H
CRCl2
O
H
CRCl2
Me3SiLi
LiO
R
Cl
H
TMS
Cl
O
H
R
TMS
Cl
+
O
H
Cl
TMS
R

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9. The calculation of Strausz and coworkers[8] suggests that the rearrangement of formylmethylene to oxirene will have an activation energy of about 19 kcal/mole. This appears to contradict experiments[3b] which suggest that oxirene formation from thermally generated alkyl substituted α-keto carbenes takes place in competition with Wolff rearrangement. In fact, the temperature dependence on product yields indicates a difference in E_a of 1.5 kcal/mole, favoring Wolff rearrangement. If the Wolff rearrangement has an activation energy of 6 kcal/mole as calculated[10] for formylmethylene, then **3** and **1** should be roughly equienergetic. This analysis assumes only small effects on the reaction energetics due to alkyl substitution.

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SELECTIVE PYROLYSIS BY MULTIPHOTON INFRARED EXCITATION (MIRE)

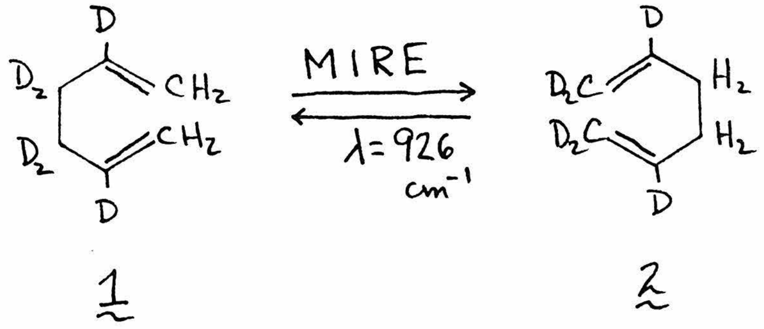
Introduction

In the past decade organic chemists became interested in the pulsed CO_2 laser and were quite excited by the prospect of performing mode-selective multiphoton infrared excitation (MIRE).[1] In spite of early claims,[2] these hopes have now for the most part fallen by the wayside; if some examples of non-ergodic, mode-specific MIRE-induced reaction are discovered in the future,[3] their generality and usefulness for the organic chemist is likely to be quite limited. At the nadir, an organic chemist surveying the field might have lamented that the IR laser looked like little more than an expensive "bunsen burner".

Out of the ashes of this fallen phoenix have recently arisen a number of extremely promising applications for organic chemistry. While mode-specific chemistry is not likely to be realized, the IR laser may prove to be a bunsen burner which offers a number of unique features. Because the diameter of the laser beam can be made smaller than that of the sample cell, it is possible to perform essentially "wall-less" thermal reactions:[4] when the sample is heated either by direct photolysis or by energy transfer from a sensitiser (such as NH_3,[5] SiF_4[6] or SF_6[7]), the energetically excited molecules lose their excess energy in collisions with other gas molecules before collision with the photolysis cell walls takes place. Recently, this feature has been taken advantage of in order to examine the "true" thermal chemistry of molecules which, in ordinary reactors, have decomposed primarily via wall-catalyzed reactions.[8] Golden and coworkers are presently preparing a new generation of the VLPP apparatus[9] which takes advantage of this particular feature of MIRE.[10]

An especially intriguing feature of the MIRE method is its ability to produce non thermodynamic product ratios by selective irradiation of the components of a gas mixture. Several examples of this have appeared in the literature. In 1975 Yogev and coworkers[11] reported that isomerization of compound **1** to produce isomer **2** could be accomplished by selective irradiation of the vinyl C-H out-of-plane bending mode of **1** (Scheme I); the wavelength of this absorption band does not overlap with any absorptions in **2**. At low pressures of **1** (5 torr), the formation of **2** from **1** was essentially quantitative even though K_{eq} is about 1 at elevated temperature. This indicates that significant heating of all of the components of the reaction mixture did not occur during photolysis. In other studies[12] simple cis/trans olefin isomerization reactions were induced by MIRE. At low pressure, conversion of the irradiated isomer to non absorbing molecules was observed; by this method it was possible to produce gas mixtures enriched in the thermodynamically less stable (irradiation transparent) component. Thus, although the chemistry displayed by the radiation absorbing species was that observed in the normal thermal reactions of those compounds, the overall reaction mixture showed distinctly non-thermodynamic, or non-equilibrium, product ratios.

Scheme I



$$K_{eq}\left(\underset{\sim}{2}/\underset{\sim}{1}\right) = 0.71\ (25°C)$$
$$0.81\ (200°C)$$

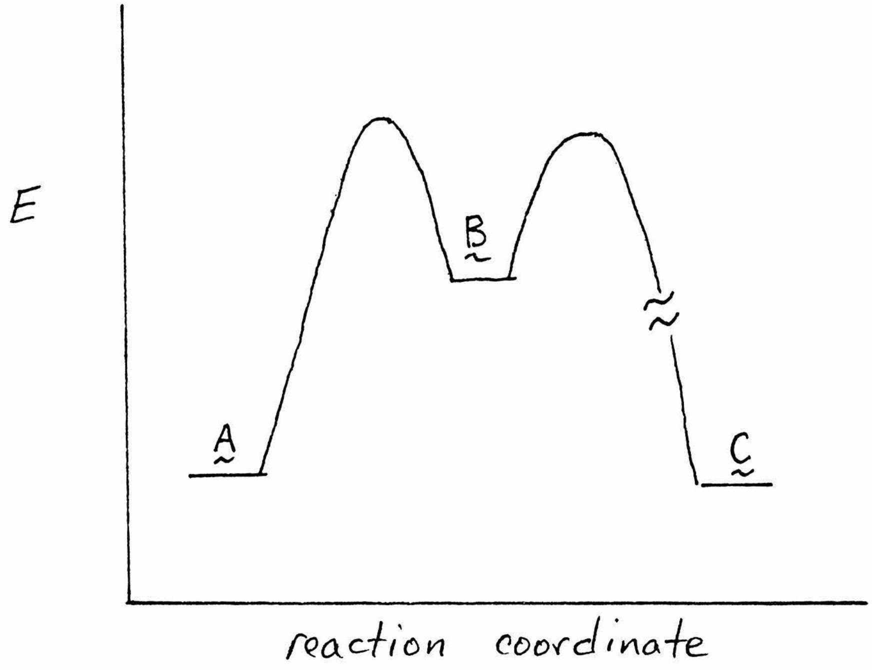


Figure 1

Proposal

It is proposed that the ability to selectively "heat" one component of a reaction mixture be utilized as part of a general scheme to produce detectable quantities of molecules (stable at near ambient temperatures (ca. 100^{o})) which, if prepared from the same precursors at elevated temperature by the usual methods (flow tube or solution reaction), would be unstable to the reaction conditions and undergo secondary reaction. A second proposal is made for the design of a preparative scale MIRE photolysis cell in which samples sufficiently large to permit isolation and characterization by normal methods (NMR, IR, mass spectroscopy) may be irradiated.

The energy diagram in figure 1 serves to illustrate a problem frequently encountered in organic chemistry: a molecule of synthetic or mechanistic interest (**B**) is the intended product of thermal reaction of a precursor molecule (**A**); however, because of the temperature required to effect reaction of **A**, **B** itself undergoes rapid (secondary) reaction to produce a different product (or products, **C**). This situation is particularly frustrating to the experimenter when it prevents the isolation of reaction intermediates or target synthetic molecules which are suspected, or known, to possess reasonable stability at room temperature. For problems of this type, pulsed IR lasers may offer special advantages. MIRE, at low pressures of reactants (ca. 1 to 10 torr), of an IR absorption band unique to **A** should induce reaction of **A** to produce **B** under conditions where the temperature of non absorbing species is moderate.[13] Temperature buildup in the non absorbing gases can be controlled by varying overall reactant pressure, the energy fluence of the incident irradiation and by adding inert bath gases to the reaction mixture. Factors limiting the application of this method include insufficient volatility of the compound to be photolyzed (which will prevent the irradiation of quantities large enough for analysis), the presence of overlapping IR absorption bands in **A** and **B**, and a low energy barrier to secondary reaction of **B**. The two examples cited below illustrate specific problems to which the unique qualities of this method might be applied.

To employ the proposed selective pyrolysis method it is critical that the temperature experienced by irradiation-transparent gases be too low to cause appreciable secondary reactions. It appears that no investigations have sought to determine the gas temperature generated upon direct irradiation of one (reacting) component of a gas mixture. This question bears directly on the minimum depth of the energy well in which the product of photolysis (**B**) must lie if secondary reactions are to be avoided. A way to evaluate this factor would be to perform the direct irradiation-induced reaction of compound **A** in the presence of a transparent molecule (**D**) of known, **lower** activation energy. The ratio of **A** reacted to the reaction of non absorbing molecule **D** would be an empirical measure of the importance of energy transfer from **A** to **D**; thus **D** will serve as an internal thermometer in the irradiation. Any molecule whose thermal chemistry is well characterized and which has an E_a in the range

50 to 70 kcal/mole would be suitable for direct irradiation-induced reaction; molecules which might be employed as internal thermometers include 1,4-cyclohexadiene ($\log_{10}A = 12$, $E_a = 43$ kcal/mole for loss of H_2) and cyclobutene ($\log_{10}A = 13.3$, $E_a = 33$ kcal/mol for ring opening to 1,3-butadiene). The relative importance of various laser parameters to the proposed selective pyrolysis technique may be evaluated by this method. It is anticipated that the presence of inert bath gases such as He, Ar or CF_4 will help to lower the temperature experienced by irradiation-transparent molecules in the irradiated zone.

With an elegent labelling experiment and kinetic analysis, Walsh and coworkers have convincingly demonstrated the intermediacy of cyclopropene in the thermal interconversion of allene and propyne.[14,15] However, because of the relative heats of formation of the molecules and the shallowness of the well in which cyclopropene lies (figure 2), cyclopropene has never been detected in the final product mixture. The energy diagram in figure 2 quite closely resembles that in figure 1 where cyclopropene (**B**), while stable to unimolecular reaction up to ca. 150° C, is unstable to the conditions of allene and propyne isomerization. By the proposed MIRE method, it may be possible to isolate the cyclopropene intermediate by direct irradiation of propyne or allene.[16]

Another problem which recently appeared in the literature occurred during the effort of de Meijere and coworkers[17] to prepare a theoretically interesting molecule (**3**, Scheme II). The synthetic route to **3** involved gas phase thermal rearrangement of

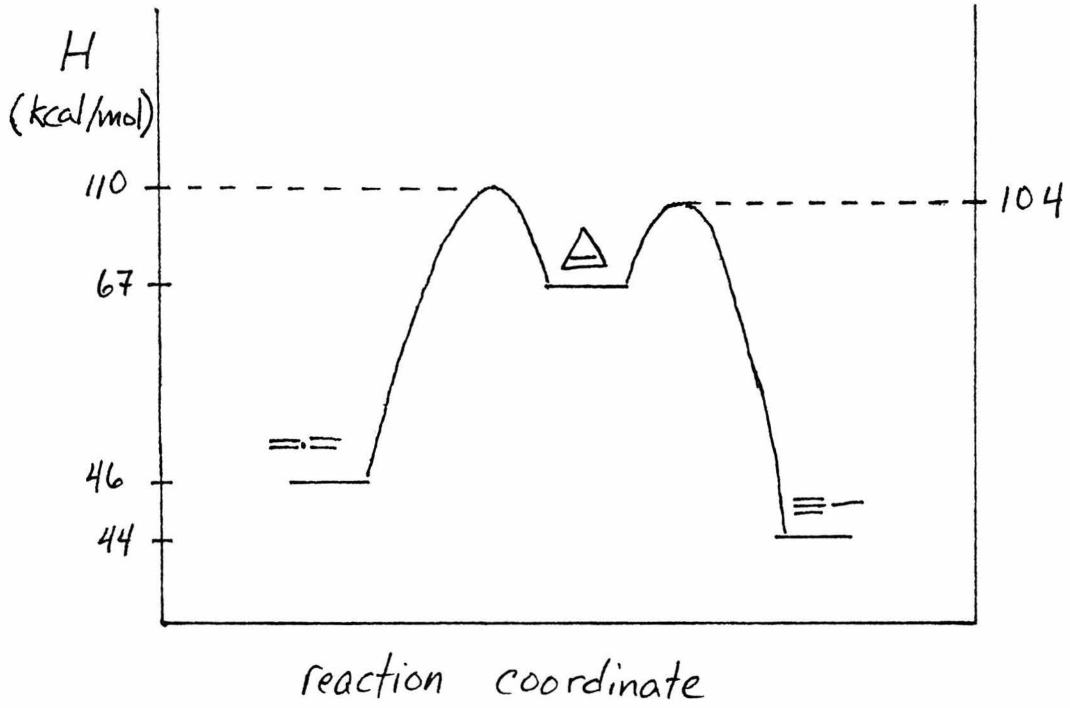
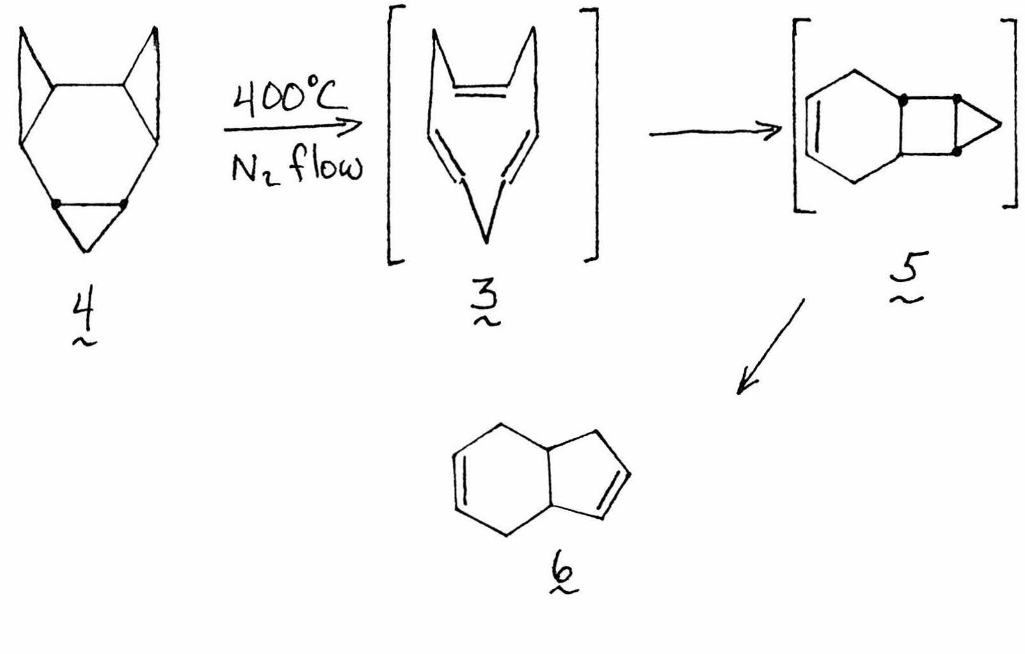


Figure 2. Enthalpy diagram for allene-propyne isomerization.[14]

Scheme II



4

3

5

6

4 as the final step. Reaction of **4** however, yielded none of the desired compound; instead, unimolecular product **6** was obtained. On the basis of labelling results de Meijere argued that **3** was formed in the reaction but was unstable to the vigorous reaction conditions. MIRE of the vinyl H absorption band of **4** should lead to rearrangement. Compound **3** is not likely to have an absorption band at the irradiation wavelength since it lacks the vinyl H moiety. As further required by the proposed selective pyrolysis technique, **3** is expected to possess reasonable thermal stability.[17] This system thus meets the basic requirements for study by this method.

In the first example discussed above the desired product, cyclopropene, is a known molecule and can be identified by VPC coinjection and mass spectral analysis. De Meijere's study, however, represents a different kind of problem, since the goal was to isolate and determine the physical properties of the target molecule. Because it is a tedious process to obtain even milligram quantities of products by MIRE using currently available techniques, there is a need for a preparative MIRE photolysis cell. One possible design for such a reactor is illustrated in figure 3. This cell is designed to allow the continuous static-vacuum transfer of a reactant (**A**) through the zone irradiated by the laser. The variables of total pressure in the cell, fluence of the beam, frequency of laser pulsing and the residence time of **A** in the cell (which may be controlled by adjusting the aperture leading from the cell to the cold trap)

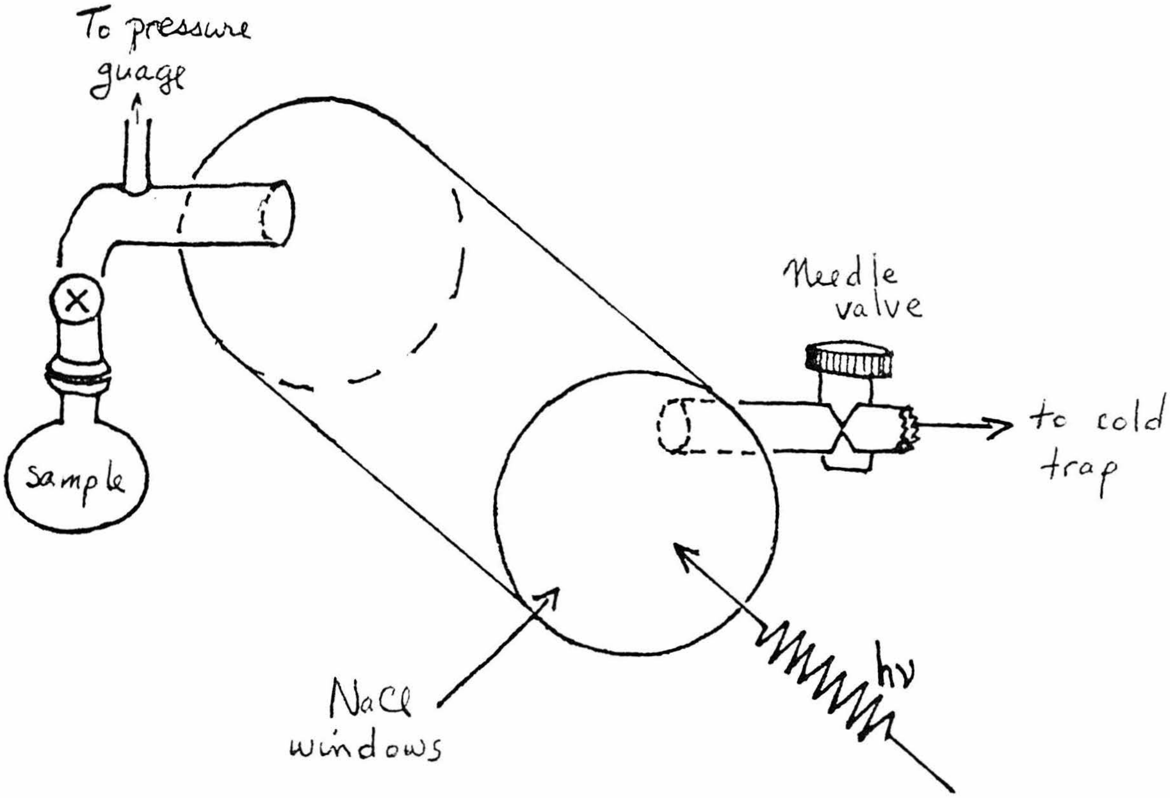


Figure 3. Design for a preparative MIRE photolysis cell.

may be varied in order to optimize conversion of **A.** With this apparatus it should be possible to subject comparatively large amounts of sample to irradiation. This design may also be used for the sensitized photolysis of large amounts of sample: if the cold trap is kept slightly above the boiling point of the sensitizer (for SiF_4, -86^{o} C at 760 torr), then it should be possible to pass the reactant through the cell (by static transfer) and observe the sensitized reaction. In sensitized photolyses the energy fluence can be turned up to fairly high levels in order to obtain substantial conversion per pulse. At the same time, the advantage of "cold reactor walls" will still be enjoyed.

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CIDNP AS A TOOL FOR THE STUDY OF THE PHOTOCHEMISTRY OF ORGANOSILICON COMPOUNDS

Introduction

While the field of silicon chemistry has been actively investigated for a number of years, many of the mechanistic aspects remain to be characterized. This is especially true of the photochemistry of silicon compounds; while the photochemical generation of silyl radicals and silylenes is of growing importance as a preparative tool,[1] numerous mechanistic questions await study. In general, the events immediately following electronic excitation of the precursors of these reactive species are not well elucidated and, with the exception of some very recent studies of silylenes,[2] the electronic excited states (singlet or triplet) involved in the formation of these reactive intermediates has not been examined.

Proposal

The technique of chemically induced dynamic nuclear polarization (CIDNP)[3] has been applied with great success to the study of organic reactions which involve radical intermediates. It is proposed that this method be used to elucidate numerous mechanistic details of the photochemical generation of silyl radicals from several different precursor molecules. Application of the CIDNP technique to photochemical silyl radical-generating reactions is likely to provide insight into the mechanism of decomposition of various silyl radical precursors. Furthermore, it should provide a method of determining the spin multiplicity of the precursor excited states leading to the formation of the radicals. This will also help to establish the role of various photochemical sensitizers, which currently are used without detailed understanding of the spin multiplicity transferred nor the mechanistic role played in the photochemical generation of silyl radicals.

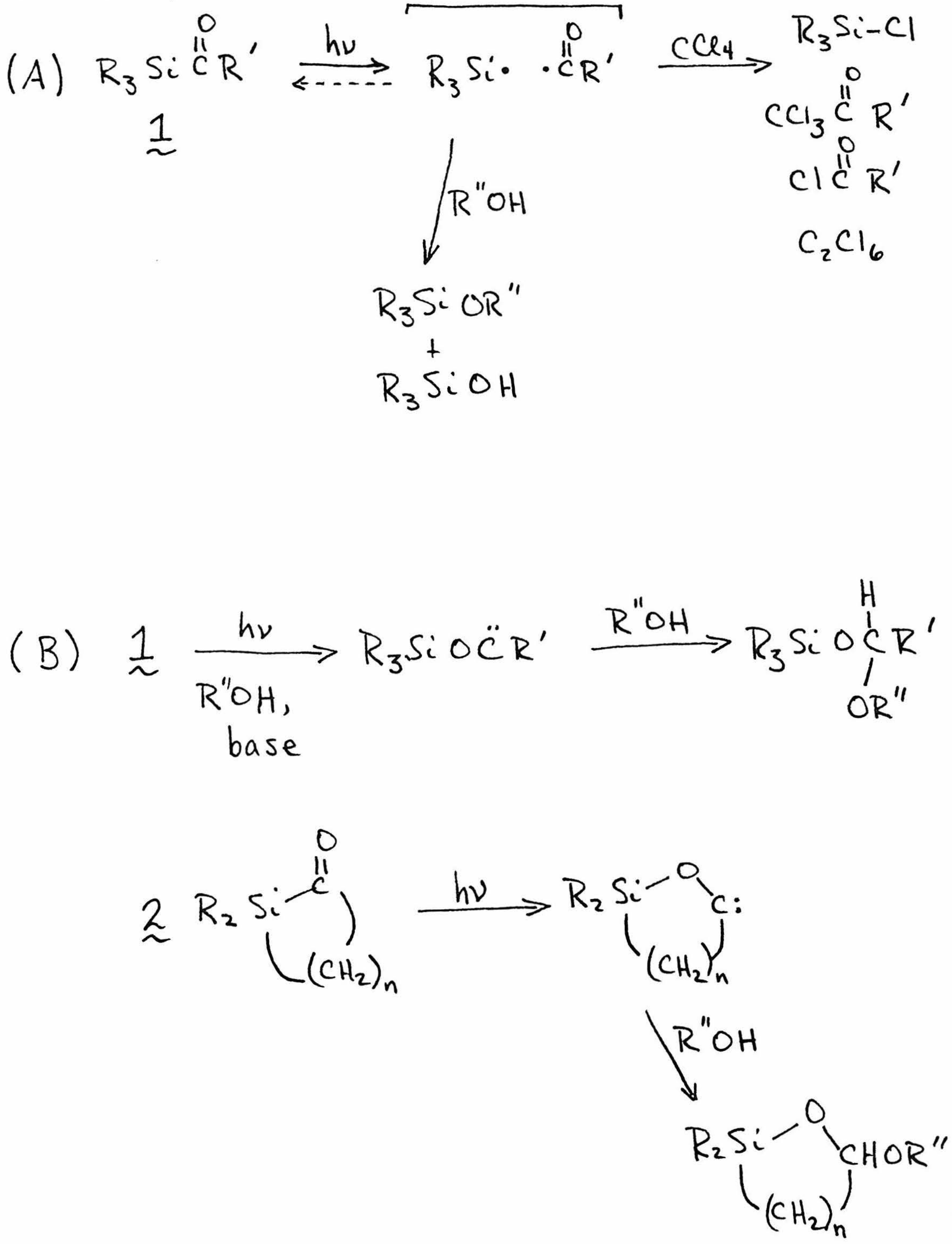
It seems likely that ^{13}C- and ^{29}Si-CIDNP will provide the greatest insight into the mechanism of decomposition of photochemical silyl radical precursors. ^{13}C-CIDNP (recorded with an FT-NMR spectrometer) has been employed on numerous occasions in the study of organic reaction mechanisms[4] and is conceptually identical to ^{1}H-CIDNP. Typically, the enhancements observed with carbon nuclei are even larger than those observed with protons. ^{29}Si-CIDNP apparently has not been recorded before. This situation may be due to the fact that silicon NMR is only lately becoming widely recorded.[5] The natural abundance of ^{29}Si (spin 1/2) is 4.7%, appreciably greater than that of ^{13}C. Complicating the recording of silicon NMR spectra, however, are long relaxation times and the presence of a negative nuclear overhauser effect. $Cr(acac)_2$ can be added to the NMR solution to reduce these problems.

Four compounds that generate silyl radicals on photolysis are shown in Schemes I through IV. The photolysis of silyl mercury compounds and silanes are widely used methods of producing silyl radicals. Determination of the excited states responsible for the direct and sensitized photochemical decomposition of these compounds and other mechanistic details are the intended goal of the proposed CIDNP investigations; the application of CIDNP to the study of each of these reactions is briefly outlined below.

In Scheme I are outlined the two major reaction pathways which have been postulated to explain the photochemical reactivity of acylsilanes (**1**). Pathway (A) is observed in a variety of organic solvents[6] and appears to involve the cleavage of the silicon acyl bond by an excited state of **1**. Products of trapping with CCl_4 strongly imply the presence of the silyl and acyl radicals. The second pathway (B) is the exclusive reaction mode of cyclic acylsilanes (**2**)[7] and is also followed when the with acyclic acylsilanes when the photochemical reaction is carried out in alcohol solvent in the presence of a trace of base.[8] In pathway (B) silicon migration to the carbonyl oxygen gives a carbene which inserts into the hydroxyl OH bond of the solvent.

The application of CIDNP to the photochemistry of acylsilanes might further elucidate several mechanistic details: (1) Evidence for the intermediacy of radical pairs in the migration of silicon to the acyl oxygen would be obtained if CIDNP (^{13}C or ^{29}Si) were observed in the acetal reaction product. (2) The possibility exists that the photochemical cleavage of **1** to give the radical pair is reversible; the observation of CIDNP in the starting material would provide evidence on this point. (3) The importance of the spin state on the photochemical

Scheme I

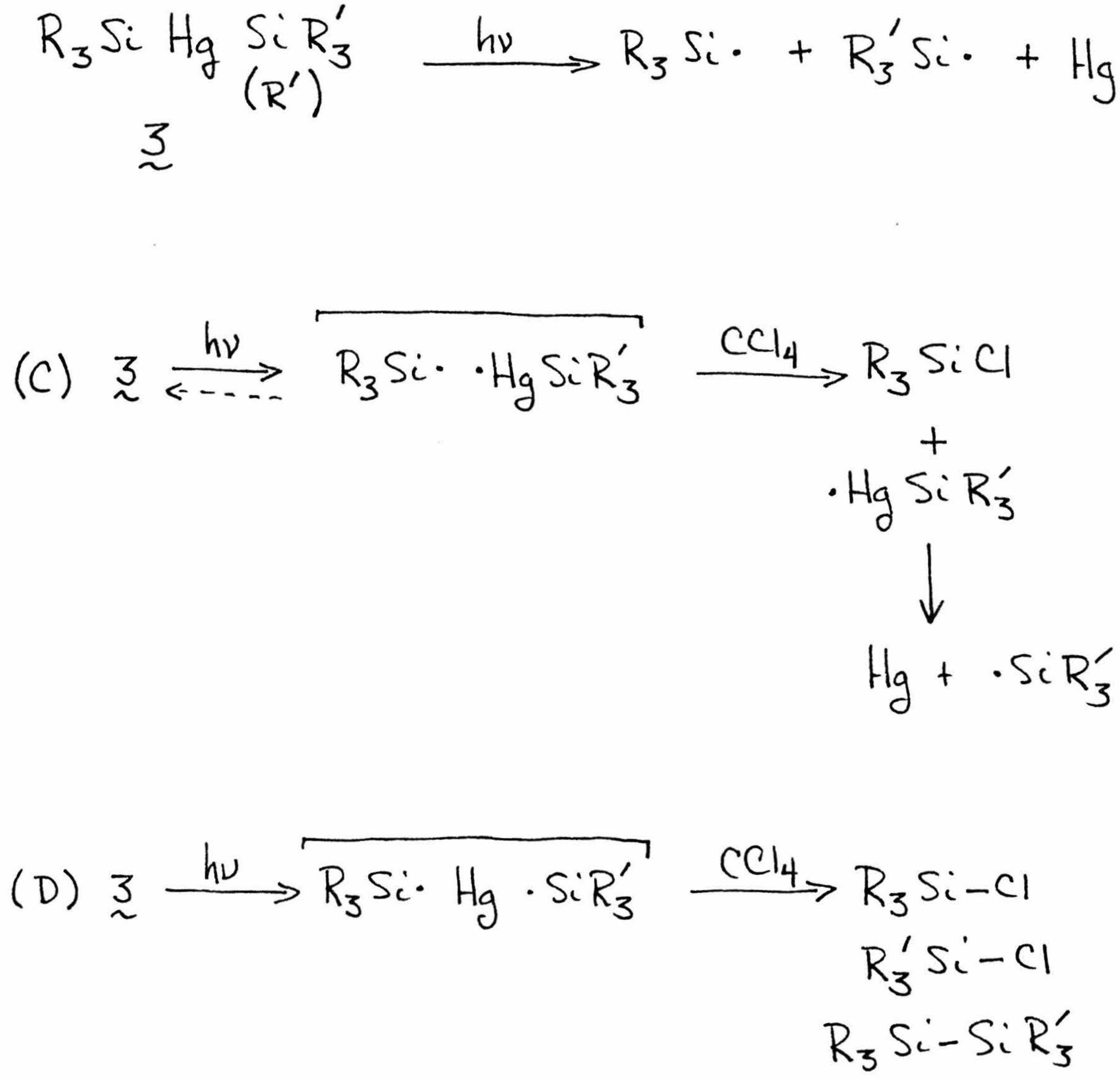

(A)
R3SiCOR'
1
hν
R3Si• •COR'
CCl4
R3Si-Cl
CCl3COR'
ClCOR'
C2Cl6
R"OH
R3SiOR"
+
R3SiOH
(B)
1
hν
R"OH, base
R3SiOC̈R'
R"OH
R3SiOCHR'
OR"
2
R2Si
(CH2)n
hν
C:
R"OH
CHOR"

reaction may be determined by CIDNP studies. The direction (absorption or emission) of the polarized signals observed in the trapping products will depend on the spin state of the radical pair formed upon photolysis.[3] Direct and sensitized photolyses may produce different excited states of **1**. It is possible that the reaction pathway followed depends on the spin multiplicity of the excited state. The use of sensitizers to effect the reaction of **1** does not appear to have been examined.

A last point that might be addressed by a CIDNP study is related to the observation that silyl radicals undergo inversion much more slowly than carbon radicals;[9] in fact, free silyl radicals in solution (generated from optically active precursors) undergo solvent trapping in competition with loss of configuration. Such an observation has been made in the photolysis of an optically active acyl silane (where the substituents on silicon were methyl, phenyl and naphthyl).[10] About 60% net retention of configuration was observed in the products of trapping with CCl_4; the product of trapping with alcohol showed about 80% net retention and the products derived from silicon migration to oxygen showed about 90% net retention. It would be interesting to examine these reactions in an NMR probe in the presence of a chiral shift reagent which could separate the signals of enantiomeric products.[11] The observation of substantial CIDNP in the products with retention of configuration[12] would dramatically confirm the configurational stability of silyl radicals. It would also allow an estimate to be made of the rate constant for inversion based on the time scale of the CIDNP phenomenon (10^{-8} to 10^{-9} seconds).[3]

In Scheme II the photochemistry of (bis)silyl mercury and silyl alkyl mercury compounds (**3**) is outlined. Photolysis of these compounds is an effective method of generating silyl radicals in solution.[13] Several mechanistic details which may be elucidated by the application of CIDNP to these reactions are the following: First, the mechanism of formation of the silyl radicals is not understood at present. Two possibilities may be enumerated: one bond cleavage (pathway C) or simultaneous two bond cleavage (pathway D). The lifetime of alkyl mercury and silyl mercury radicals in solution are believed to be very short; this has prevented their detection by ESR spectroscopy. CIDNP observed in compound **3** would indicate that decomposition must occur as shown in equation (**C**) and that cage combination of the radical pair is possible. This observation would establish the finite lifetime of the mercury radical and would even allow a rough estimate of its lifetime. The direction of the polarizations observed in reaction products (such as silyl chlorides for reactions performed in the presence of halogenated solvents) will depend on whether the radical pair of pathway (C) or (D) is present. The difference in g factors for silyl and mercury radicals[14] should be large enough to produce a net effect in the reaction products; the direction of polarization is determined by the g factor difference. The g factor difference for paired trimethylsilyl radicals (pathway (D)) will be zero for R = R'; thus polarization will be weak and should show a

Scheme II



$$\underset{\underset{\sim}{3}}{R_3Si\,Hg\,\underset{(R')}{SiR'_3}} \xrightarrow{h\nu} R_3Si\cdot + R'_3Si\cdot + Hg$$

$$(C)\quad \underset{\sim}{3} \underset{\leftarrow - - -}{\xrightarrow{h\nu}} \overline{R_3Si\cdot \;\; \cdot HgSiR'_3} \xrightarrow{CCl_4} R_3SiCl + \cdot HgSiR'_3$$

$$\cdot HgSiR'_3 \longrightarrow Hg + \cdot SiR'_3$$

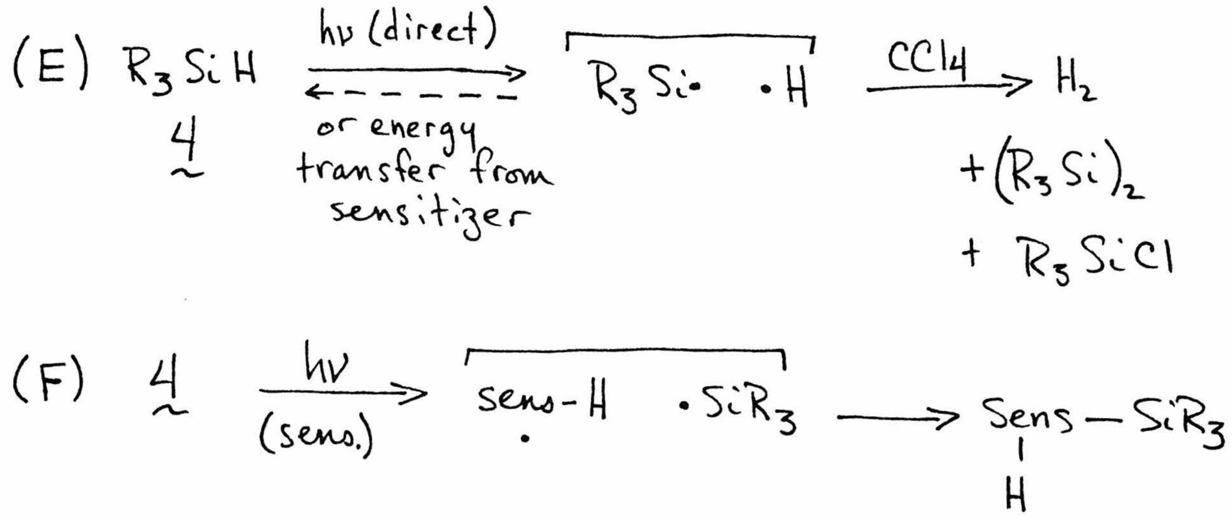
$$(D)\quad \underset{\sim}{3} \xrightarrow{h\nu} \overline{R_3Si\cdot \;\; Hg \;\; \cdot SiR'_3} \xrightarrow{CCl_4} \begin{matrix} R_3Si-Cl \\ R'_3Si-Cl \\ R_3Si-SiR'_3 \end{matrix}$$

multiplet effect. The g factor of silyl radicals depends strongly on the groups bonded to silicon;[14] thus photolysis of asymmetric mercury compounds may lead to CIDNP signals even if decomposition occurs by pathway (D).

A second piece of information that may be obtained concerning the photochemical decomposition of these mercurials is the effect of photochemical sensitisers on the spin state of the radical pairs generated. There could conceivably be a change in decomposition mechanism ((C) vs (D)) depending on the spin state of the precursor.

Direct photolysis of phenyl substituted silanes (**4**) leads to cleavage of the silicon hydrogen bond.[15] In the absence of the phenyl chromophore silicon-hydrogen bond cleavage may be induced by irradiation of elemental mercury,[16] acetone[17] and benzophenone[18] sensitizers. Two mechanisms which have been proposed to explain these reactions are illustrated in Scheme III. The mercury sensitized photolysis has been explained by both mechanisms; the ketone "sensitized" reactions are usually described by pathway (F). Pathway (E) is intriguing because analogous homolytic cleavage of carbon hydrogen bonds by UV photolysis is unknown. It would therefore be unusual to observe CIDNP arising from the hydrogen-silyl radical caged pair shown in pathway (E). CIDNP studies could confirm the presence of the radical pair and also provide information as to the occurrence of cage recombination to regenerate **4**. The spin state of the radical pair generated upon direct and sensitized photolysis may

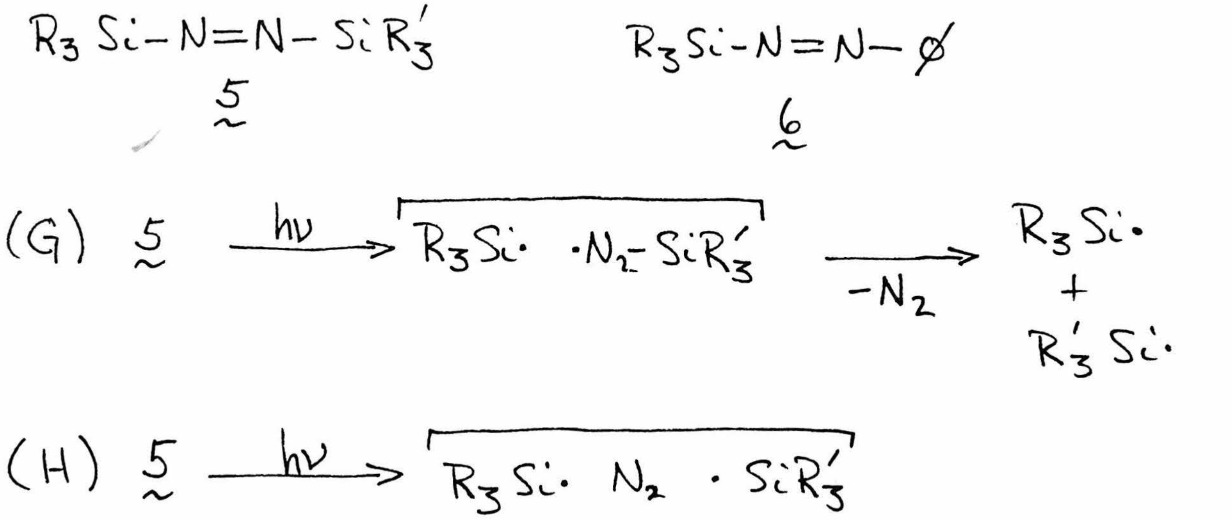
Scheme III



$$\text{(E)}\quad \underset{\underset{\sim}{4}}{R_3SiH} \xrightleftharpoons[\text{or energy transfer from sensitizer}]{h\nu\text{ (direct)}} \overline{R_3Si\cdot \quad \cdot H} \xrightarrow{CCl_4} H_2 + (R_3Si)_2 + R_3SiCl$$

$$\text{(F)}\quad \underset{\sim}{4} \xrightarrow[\text{(sens.)}]{h\nu} \overline{\underset{\cdot}{\text{sens}}\text{-}H \quad \cdot SiR_3} \longrightarrow \underset{\underset{H}{|}}{\text{Sens}} - SiR_3$$

Scheme IV



$$\underset{\underset{\sim}{5}}{R_3Si-N{=}N-SiR'_3} \qquad\qquad \underset{\underset{\sim}{6}}{R_3Si-N{=}N-\phi}$$

$$\text{(G)}\quad \underset{\sim}{5} \xrightarrow{h\nu} \overline{R_3Si\cdot \quad \cdot N_2\text{-}SiR'_3} \xrightarrow[-N_2]{} R_3Si\cdot + R'_3Si\cdot$$

$$\text{(H)}\quad \underset{\sim}{5} \xrightarrow{h\nu} \overline{R_3Si\cdot \quad N_2 \quad \cdot SiR'_3}$$

be determined by the CIDNP observed in the products of the reaction. Evidence for pathway (F), in which reaction is induced by abstraction of hydrogen by the sensitizer, would be found if CIDNP were observed in the ^{1}H- or ^{13}C-NMR spectra of the sensitizers.

The last photochemical reaction to be discussed is the reaction of (bis)silyl azo (**5**) and phenyl trialkylsilyl azo compounds (**6**, Scheme IV). Compounds **5**, unlike organic azo compounds, undergo bimolecular reactions on thermolysis.[19] Photolysis, however, produces silyl radicals.[20] Compound **6** generates free silyl radicals either upon photolysis or heating[21] at 115°C. The photochemical reactions of these compounds are formally similar to that of organic azo compounds and raises the question as to whether or not the same general rules of one bond versus simultaneous two bond cleavage apply. CIDNP has been very effectively employed to elucidate organic azo decomposition mechanisms;[22] similarly, monitoring the photolysis of ^{15}N labelled **5** and **6** by ^{15}N-NMR for polarization of the nitrogen atoms would provide evidence for the presence of stepwise cleavage (G). The simultaneous bond cleavage pathway (H) may produce CIDNP in the reaction products if R is different from R' in **5**. Again, it would be interesting to examine the effect of sensitizers on the homolysis reaction.

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INVESTIGATIONS IN ORGANOMETALLIC PHOTOCHEMISTRY

Introduction

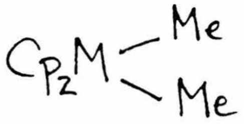
The field of organic photochemistry commands the attention of organic chemists precisely because the photochemical reactivity displayed by organic compounds frequently differs substantially from that observed in thermal reactions. The novel photochemical reactions have proven to be fascinating mechanistically and, most importantly, permit a number of useful synthetic transformations to be carried out which do not occur upon simple heating. In comparison to organic photochemistry, the field of organometallic photochemistry is still very much in its infancy. Certainly, the possibility that unique photochemical reactions may occur is a compelling reason for intensive investigation of this field.

Only a few general classes of organometallic photochemical reactions have been characterized thus far (Scheme I). The most widely investigated is the labilization of CO ligands upon irradiation with UV light.[1] This appears to be the primary photochemical process in almost all CO containing complexes studied thus far. Typically, loss of CO is also the lowest energy unimolecular process and is observed thermally. Because the photochemical reaction can be performed at, or below, ambient temperature, thermally unstable products sometimes can be isolated and bimolecular processes which may obscure the unimolecular thermal reaction can be avoided. Similar to the CO labilization reaction, ethylene appears to be photolabile in at

Scheme I

(1) $$M-CO \xrightarrow{h\nu} M + CO$$

(2) $$\begin{tikzcd}(CO)_nM-M(CO)_n \arrow[r, "h\nu"] & 2(CO)_nM\cdot \arrow[d, "CCl_4"] \\ & (CO)_nM-Cl\end{tikzcd}$$

(3) 

$$Cp_2M{<}^{Me}_{Me} \xrightarrow{h\nu} Cp_2M + 2\,CH_3\cdot$$

$M = Ti, Zr, Hf$

(4) $$Ir\,Cl\,H_2(P\phi_3)_3 \xrightarrow{h\nu} H_2 + IrCl(P\phi_3)_3$$

(5) $$Cp'\,Ta(Cl)_3CH_2SiMe_3 \xrightarrow{h\nu} Cp'TaCl_3 + \dot{C}H_2SiMe_3$$

$(Cp' = C_5Me_5)$

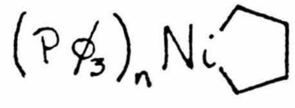
least some complexes.[2] Another well-studied photochemical process is the homolytic cleavage of metal-metal bonds in binuclear (and polynuclear) organometallic complexes.[3]

While the reactions described above have proven to be both general in nature and of some utility in preparative chemistry, it is likely that they represent only a fraction of the photochemical reactivity of organometallic complexes. Because CO labilization dominates the photochemistry of metal carbonyl complexes, new modes of photochemical reactivity are most likely to be found in CO-free organometallic complexes. Surprisingly, there has been very little investigation of the photochemistry of complexes which do not contain CO as a ligand. Several examples which have been observed are shown in Scheme I. Photolysis of n^5-Cp_2TiMe_2 (equation (3)) appears to generate methyl radicals in the primary photochemical event,[4] although the reaction is not clean and remains somewhat poorly characterized. As outlined in equation (4), elimination of H_2 from the iridium dihydride complex is a facile photochemical process; similar thermal reactivity is not observed even after prolonged heating at 150^o C.[5] Photochemical cleavage of the tantalum silylmethyl bond has also been observed (equation (5)).[6] Thus, the few photochemical investigations of CO-free organometallic complexes that have been reported demonstrate that interesting reactivity may take place. These observations strongly encourage additional investigation of non-CO containing complexes. Again, in analogy with investigations in organic chemistry, it is hoped that these studies will result in the discovery of novel and useful molecular transformations.

Proposal

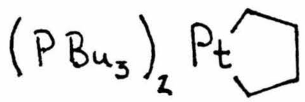
As discussed in the preceding section, the study of the photochemistry of organometallic complexes promises to reveal unusual and, hopefully, useful modes of reactivity. Outlined in this section is a general program for the study of organometallic complexes (metallacyclopentanes), compounds which are likely to display unusual reactivity.[7] It is proposed that the photochemistry of complexes **1** through **5** be determined. These compounds have been characterized previously[8-12] and in most cases their thermal chemistry has been examined. Some of the molecules undergo thermal decomposition at ambient temperature; irradiation at low temperature, however, should eliminate complications due to thermal reaction. These complexes have been selected because, a priori, several different modes of reactivity seem possible for each. It would be interesting to look for reactivity dependence on the wavelength of the incident radiation[13] (reflecting the nature of the electronic transition).

If the primary photochemical process in complexes **1** through **5** is metal-carbon bond homolysis (in analogy with the photochemistry of Cp_2TiMe_2) unusual reactivity may result because the alkyl radical will still be bound to the metal. In addition, acyl complex **4** has several possible points of bond homolysis. Examination of the photochemistry of complexes **1** through **5** may not only provide novel examples of the excited state chemistry of organometallic complexes, but may also provide a unique

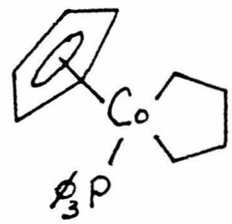


n = 2,3

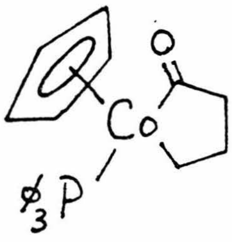
1



2



3



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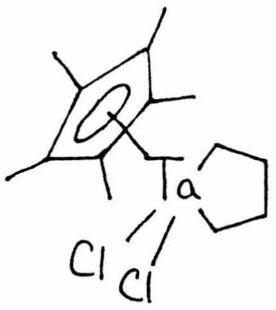


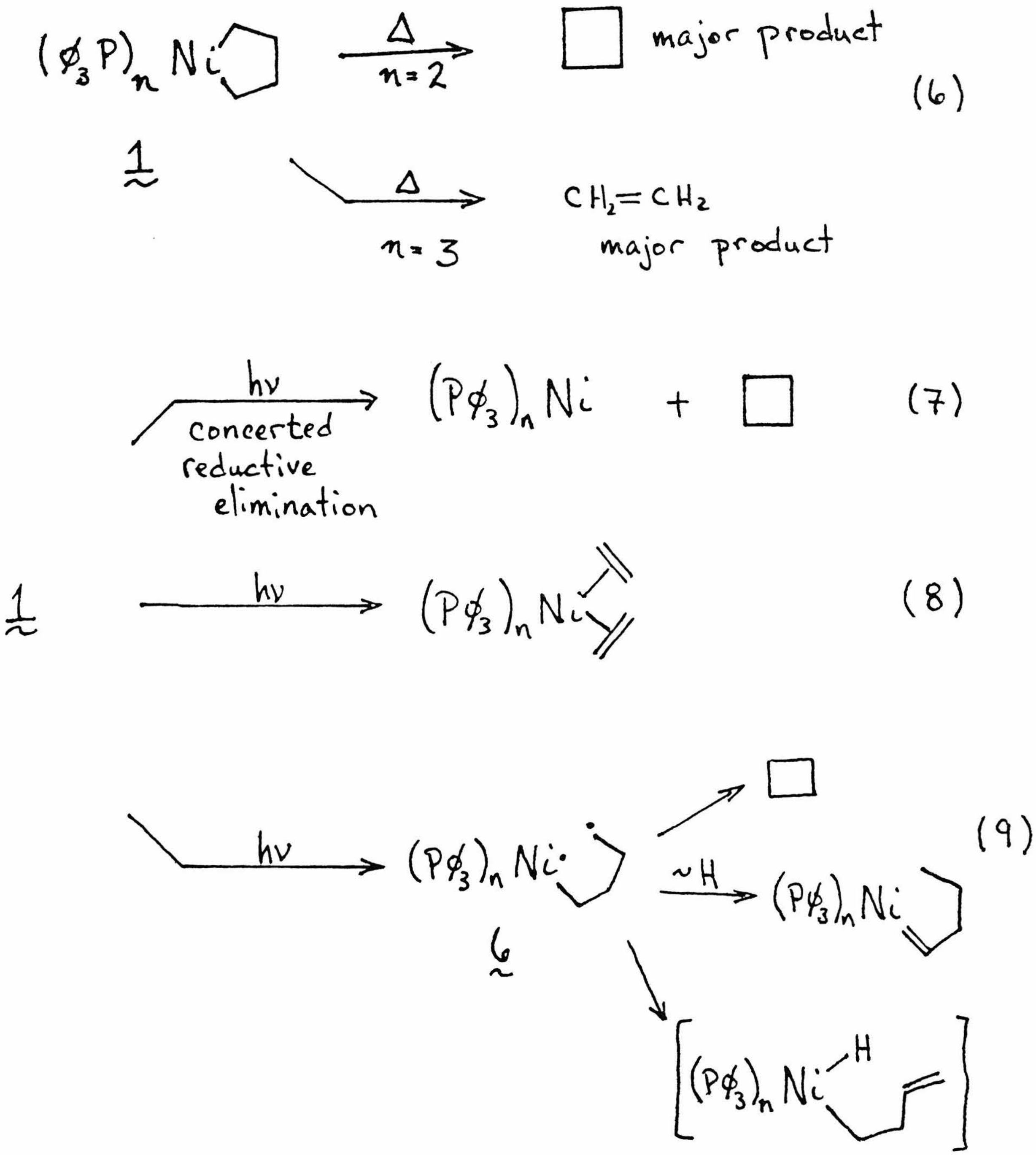
5

opportunity to examine the dynamics of reaction of unusual metal alkyl "biradicals". Possible reaction modes of several of the complexes are outlined in Schemes II through V and are discussed below. The photoreactions postulated are necessarily speculative; likely primary photochemical processes and some of the interesting rearrangements which may follow are outlined in the schemes.

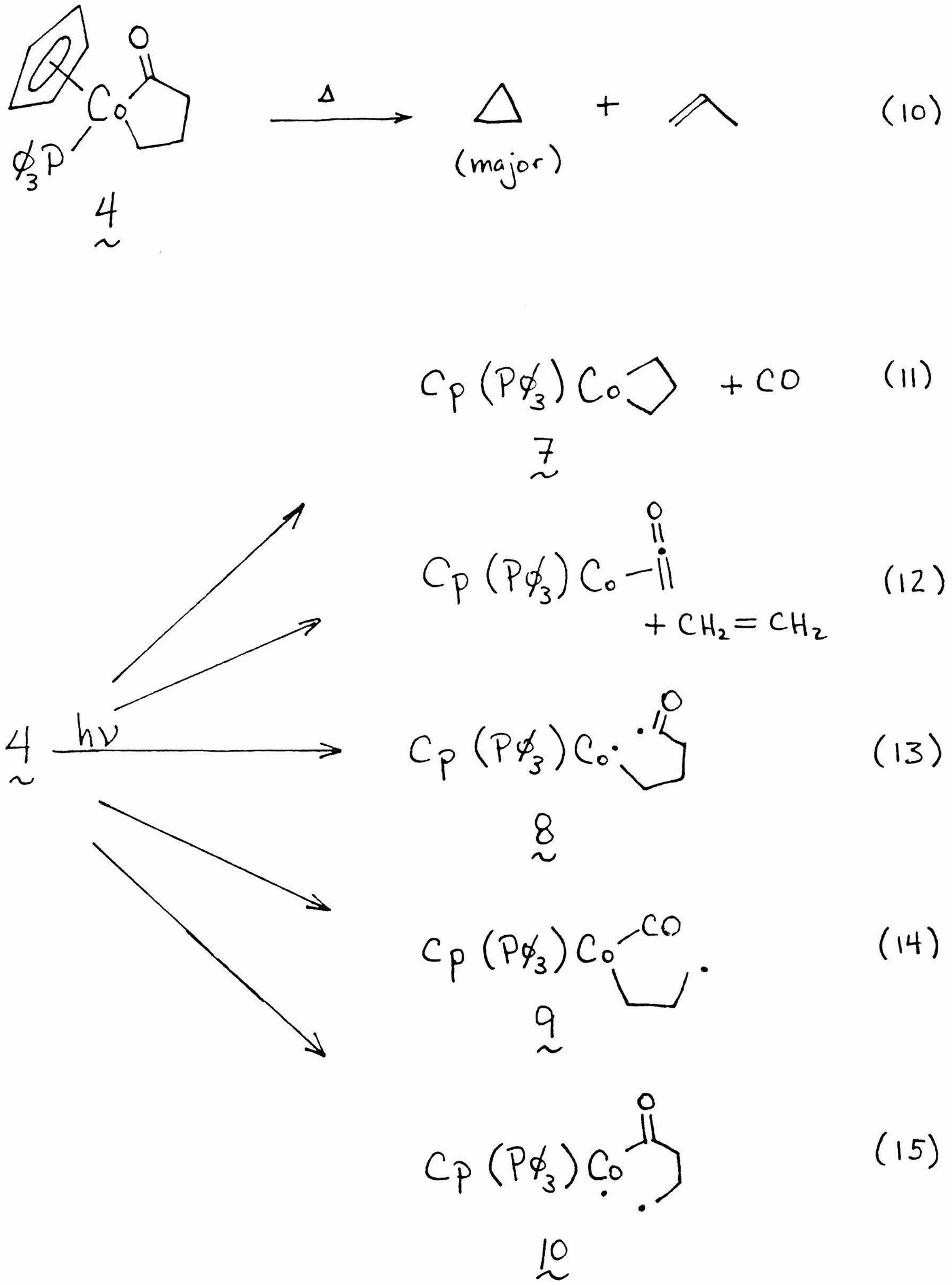
The thermal reactions of (bis)triphenylphosphine and (tris)triphenylphosphine metallocyclopentane complexes **1** have been characterized in elegant experiments by Grubbs and coworkers[8] (Scheme II). Thermal reactivity proved to be dependent on the number of phosphine ligands attached to nickel. Electronically excited **1** may simply repeat the thermal chemistry or it may explore new reaction pathways. Several possible photochemical reaction channels are outlined in Scheme II; most interesting are those in equation (9) which involve initial nickel-carbon bond cleavage to give **6** and may be followed by any of several conceivable reaction pathways.

Cobaltacyclopentanone **4** has recently been prepared in these laboratories[9] and produces a mixture of cyclopropane and propylene on thermolysis (Scheme III). Five conceivable primary photochemical processes are outlined in Scheme III. Especially interesting would be light-induced elimination of CO (equation (11)) to give cobaltacyclobutane **7**, a molecule which has thus far eluded synthesis. Equations (13), (14) and (15) outline several possible homolysis pathways; (13) and (14) are analogous to the

Scheme II


(ϕ3P)n Ni
1
Δ
n=2
major product
(6)
Δ
n=3
CH2=CH2
major product
hν
concerted
reductive
elimination
(Pϕ3)n Ni
+
(7)
1
hν
(Pϕ3)n Ni
(8)
hν
(Pϕ3)n Ni
6
(9)
~H
(Pϕ3)n Ni
(Pϕ3)n Ni
H

Scheme III

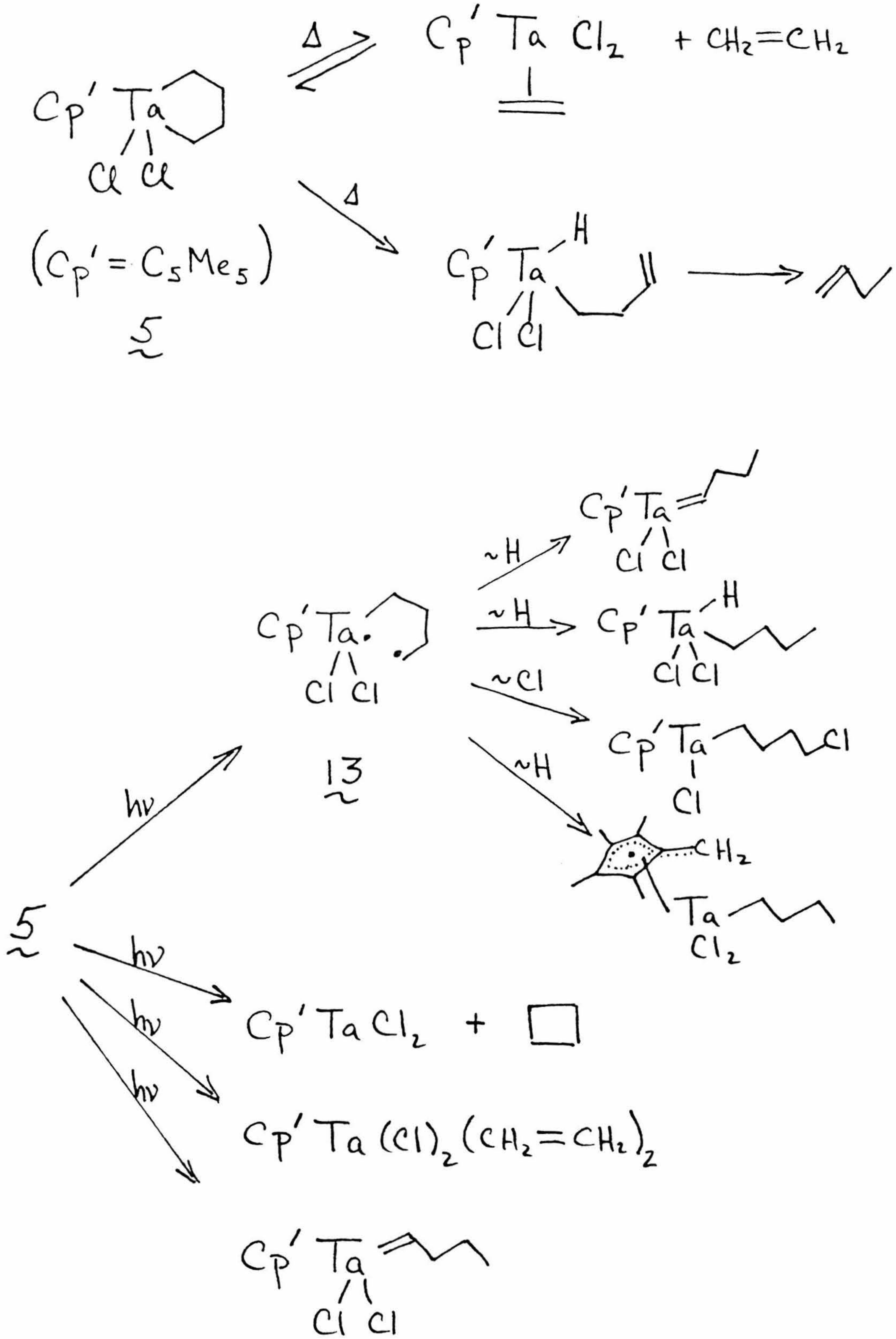

ØP
3
Co
O
4
Δ
(major)
+
(10)
Cp (PØ3) Co
+ CO
(11)
7
Cp (PØ3) Co
O
+ CH2 = CH2
(12)
4
hν
Cp (PØ3) Co·
O
(13)
8
Cp (PØ3) Co
CO
(14)
9
Cp (PØ3) Co
O
(15)
10

Norrish photochemical cleavage observed in ketones. As outlined for the biradicals in equation (9) and, again, in analogy to the reactivity of biradicals generated by Norrish photocleavage, intramolecular hydrogen transfer and cyclization reactions may be possible.

Upon heating, tantalum metallacycle **5** undergoes reversible exchange with ethylene and more slowly produces 1-butene.[10] For electronically excited **5**, several pathways may be possible (Scheme IV). It is intriguing to consider the possibility that Ta-carbon bond homolysis (equation (17)) could be followed by intramolecular chlorine transfer to the alkyl-centered radical. $Cp'TaCl_2$ is believed to form metallacycle complex **5** under an ethylene atmosphere and it is conceivable that performing the photolysis of **5** under ethylene would lead to a catalytic conversion of ethylene to the photochemical products. This would require that the final step of the photochemical reaction generate a free organic molecule and $Cp'TaCl_2$ or $Cp'TaCl_2$(olefin) which could react with more ethylene to reenter the cycle.

Mechanistic investigations of the photochemistry displayed by these compounds will be aided by deuterium labelling of the metallacycles. Further details may be elucidated by trapping unsaturated organometallic intermediates (with added 2-electron donor ligands such as phosphines and also with solvents such as CCl_4 which may trap odd-electron organometallic intermediates[14]). It may be possible to trap some of the intermediates containing alkyl radical fragments by adding radical scavengers such as hydrogen donating molecules.

Scheme IV



(16)

(17)

(18)

(19)

(20)

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(b) Strohmeier, W.; von Hobe, D.; *Z. Phys. Chem. (Frankfurt am Main)*, **1962**, *34*, 393. These results are considered in detail in reference (1), pp. 68 to 74. (c) Rest, A. J.; Sodeau, J. R.; *Chem. Commun.*, **1975**, 696.

14. See reference (1) pp. 81-87.

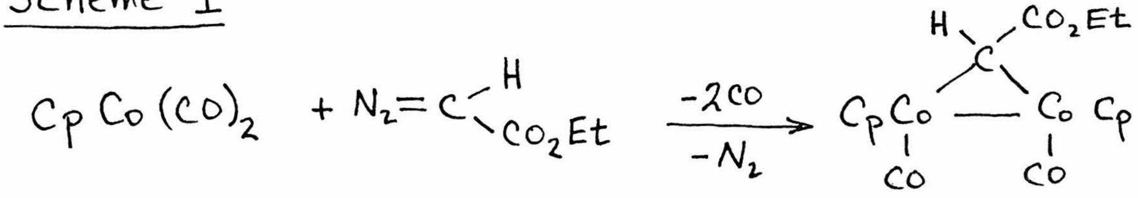
A NOVEL SYNTHETIC ROUTE TO BINUCLEAR ORGANOMETALLIC COMPOUNDS CONTAINING A BRIDGING METHYLENE FUNCTION

Introduction

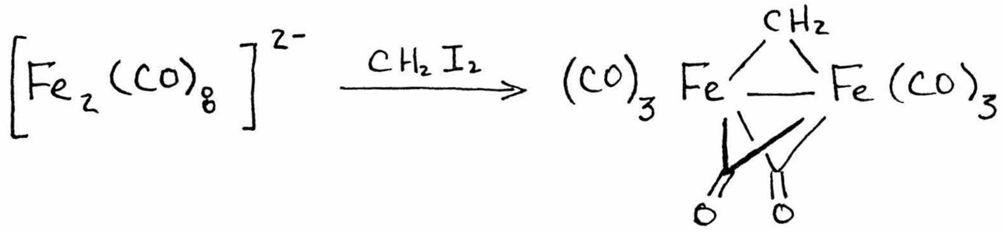
Although the first binuclear organometallic compound containing a bridging methylene group was prepared in 1969,[1] only in the past five years has interest in these molecules become widespread.[2] Interest in these compounds is due to their structural novelty and the possibility that they may display unique reactivity. One unusual characteristic is that, although formally related to metallocarbenes, bridging methylene complexes show much greater kinetic (and perhaps thermodynamic) stability.[3] Another intriguing feature of these molecules is that they belong to a small group of metallacycles containing two metals in the ring.[4] It has been noted that methylene bridged binuclear complexes may be analogues of intermediates formed on the surface of Fischer-Tropsch catalysts.[5]

In spite of the activity to prepare and study various representatives of this class of compounds, the synthetic routes discovered to date remain limited in applicability. Several metal complexes react with diazo compounds to give bridging methylene complexes (Scheme I), but the number prepared by this route remains small.[1,2a,e,f] A synthetic route recently discovered in two laboratories employs the reaction of diiodomethane with anionic binuclear complexes (Scheme II).[2h,k] The generality of this route is likely to be limited by the number of appropriate anionic binuclear complexes which may be

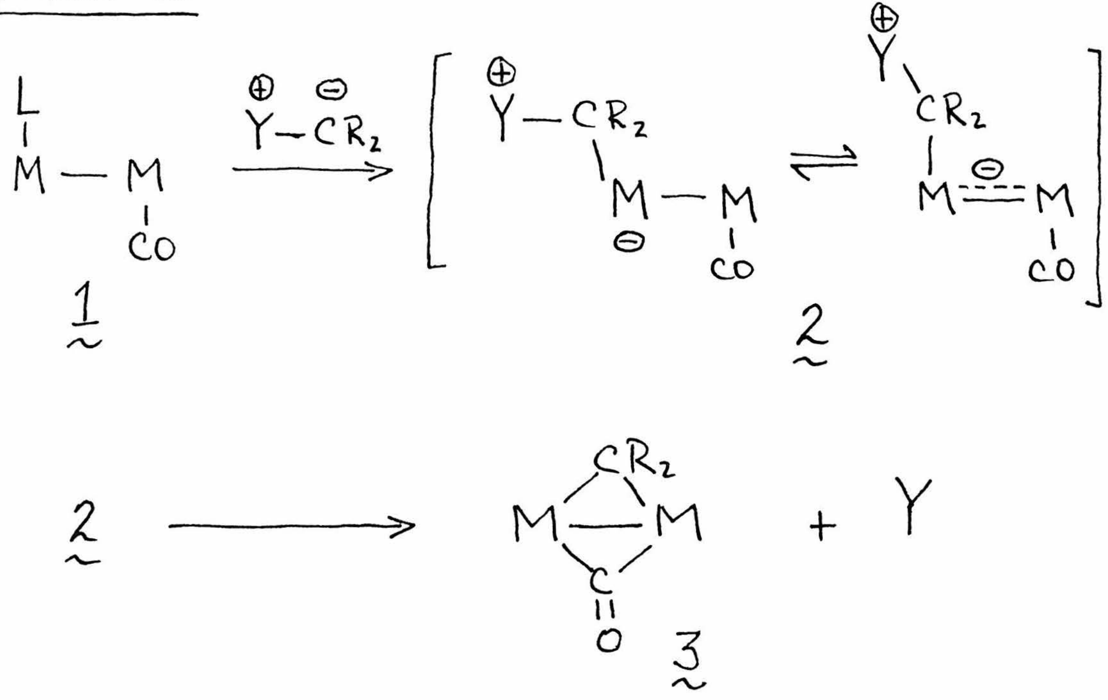
Scheme I



Scheme II



Scheme III



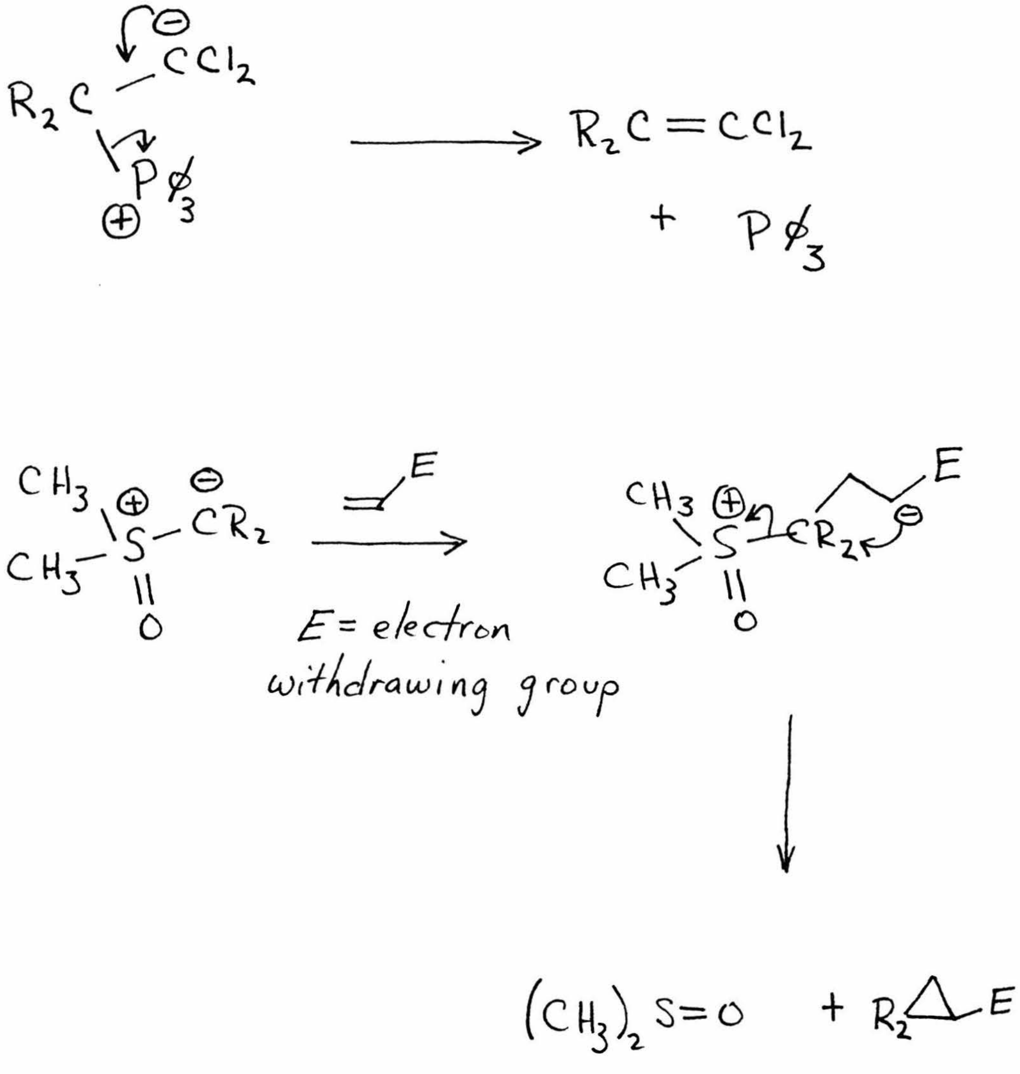
prepared. In this proposal a novel synthetic approach to methylene bridged binuclear complexes is outlined; the method could prove to be more general than those previously employed.

Proposal

The proposed synthetic route to bridging methylene complexes involves the displacement of an appropriate substituent in a binuclear complex by a phosphorus or sulfur ylid.[6] In Scheme III the general reaction sequence is outlined for the attack of an ylid ($Y^+CR_2^-$) on a binuclear complex (**1**) containing a leaving group, L, and a CO ligand which may bridge the two metals in the final product. The betaine (**2**) may eliminate the neutral phosphine or sulfur compound to give a methylene complex (**3**). Similar phosphine eliminations have been observed in both organophosphorus and sulfur betaines (Scheme IV).[7]

The reaction of ylides with numerous mononuclear organometallic complexes has been studied. Examples of the displacement of CO,[8] weakly bound olefins[9,10] and tetrahydrofuran[10] all have been reported. Such reactions have been carried out on a number of carbonyl and cyclopentadienyl complexes of the group VI, VII and VIII transition metals (Cr, Mo, W, Mn, Re, Fe, Co, Rh, Ni, Pd) with phosphorus ylides;[8,10] a similar displacement using a sulfur ylid has also been reported.[9] Alkyl, olefin and phenyl substituted phosphorus ylides all have been observed to undergo ligand displacement reactions;[8c] thus it may be possible to prepare a variety of bridging methylene groups

Scheme IV



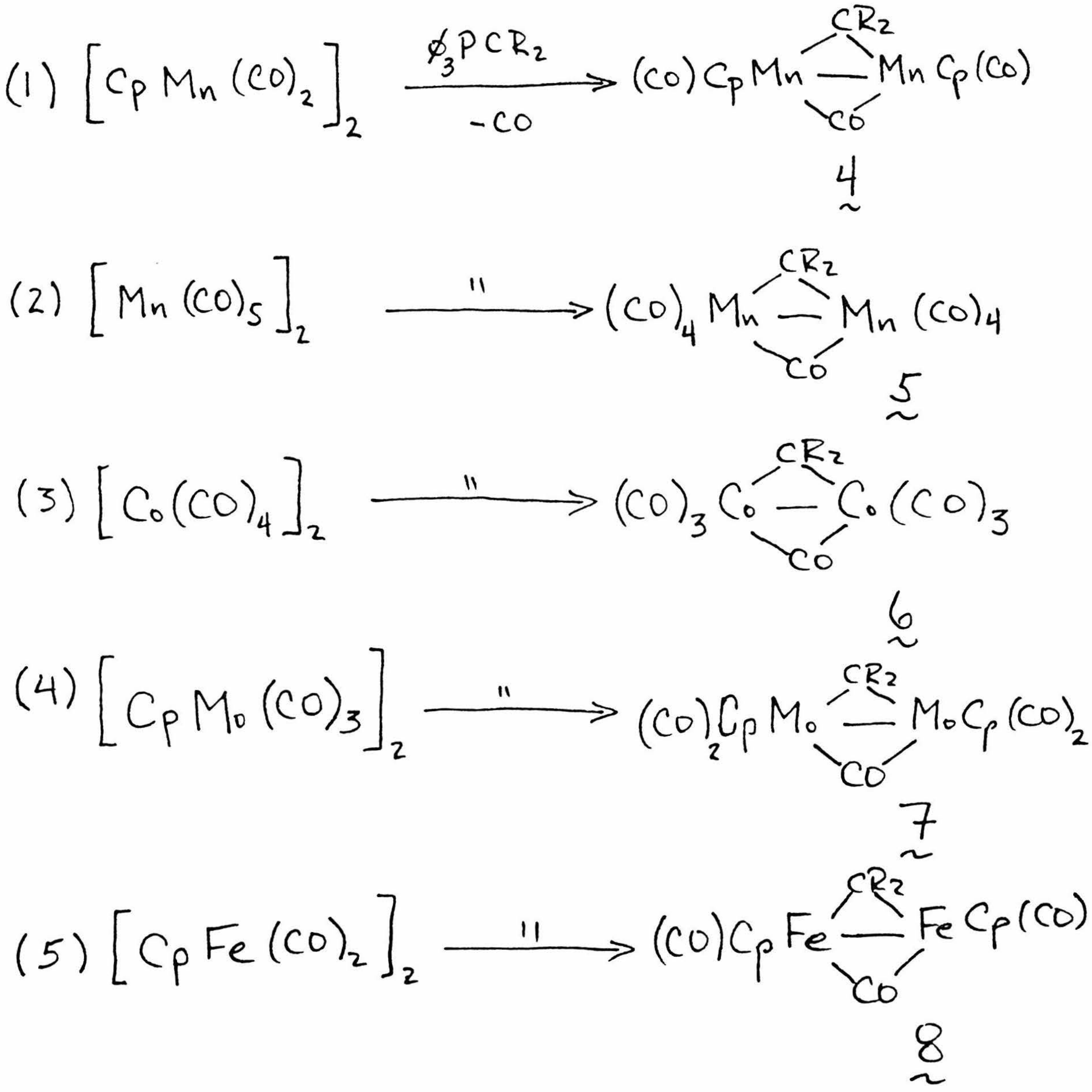
R₂C—CCl₂
Pφ₃
R₂C=CCl₂
+ Pφ₃
CH₃
CH₃
S
O
CR₂
E
E = electron withdrawing group
(CH₃)₂S=O
+ R₂ E

(eg., CR^1R^2) by this synthetic method.

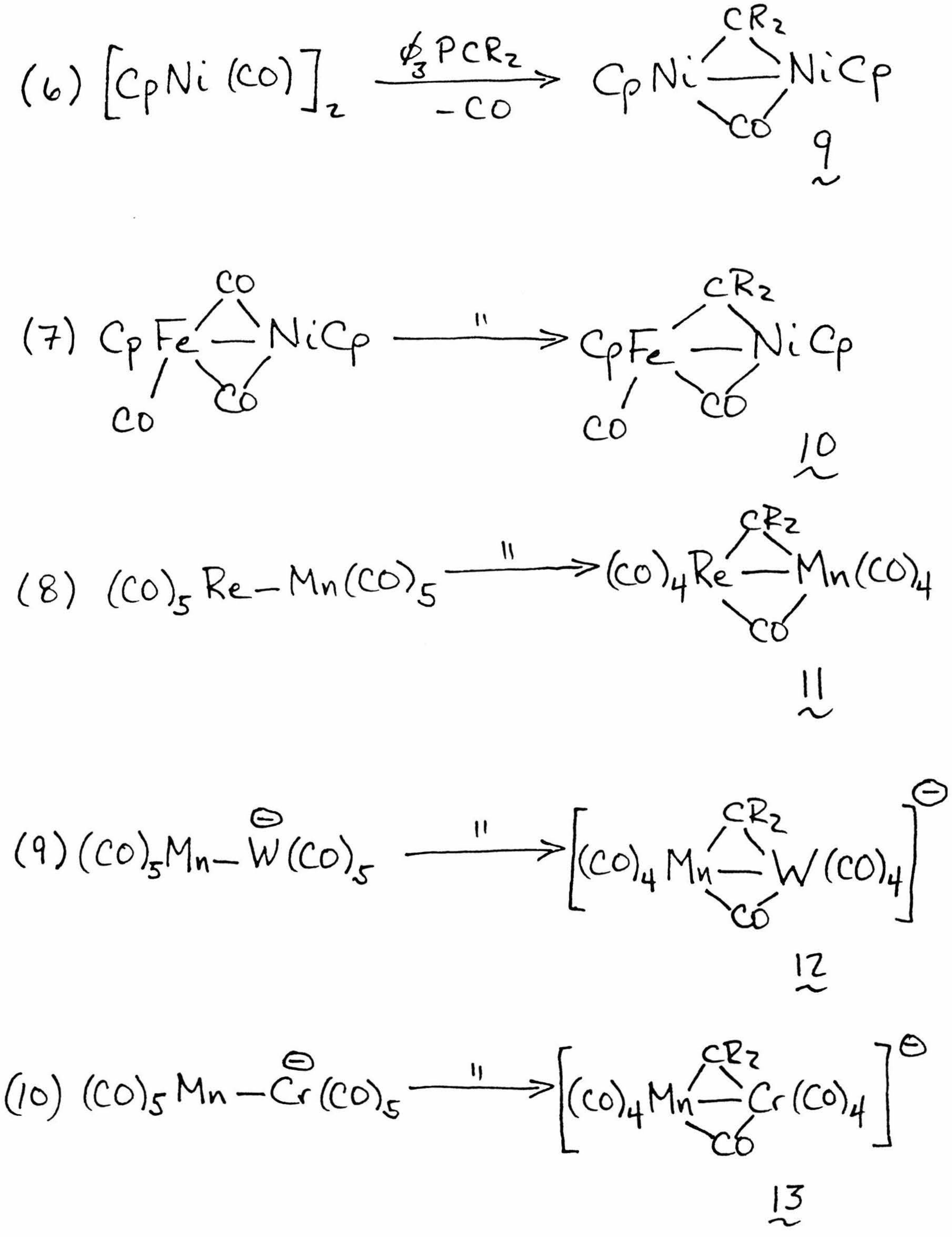
In Scheme V are given several examples of the application of this method to the preparation of binuclear bridging methylene complexes. Reaction (1) would produce a bridging methylene complex (**4**) previously prepared by Hermann and coworkers (R = H),[2a] and would provide a good initial test of the method. The nonacarbonyl dimanganese complex (**5**) has not been reported. The remaining examples (reactions (3) to (6)) illustrate the potential of this method for the synthesis of numerous, previously unavailable methylene complexes. The binuclear complexes chosen represent each of the group VI, VII and VIII triads. In all cases, the starting binuclear complexes are well characterized and readily available.

Bridging methylene-substituted binuclear complexes containing two different transition metals may also be synthetically accessible by this route. Several well characterized mixed binuclear complexes which may react with ylides to form bridging methylene complexes are also shown in Scheme V (reactions (7), (8), (9), (10)). The latter two reactions would involve anionic complexes; this could hinder substitution of ylid for CO. Elimination of triphenyl phosphine from the intermediate betaine, however, may be especially facile in these cases. Because the resultant bridging methylene complexes (**12, 13**) would be negatively charged, they may be particularly conducive to subsequent functionalization.

Scheme V


(1) [CpMn(CO)2]2
ØPCR2
-CO
(CO)CpMn—MnCp(CO)
CR2
CO
4
(2) [Mn(CO)5]2
"
(CO)4Mn—Mn(CO)4
CR2
CO
5
(3) [Co(CO)4]2
"
(CO)3Co—Co(CO)3
CR2
CO
6
(4) [CpMo(CO)3]2
"
(CO)2CpMo—MoCp(CO)2
CR2
CO
7
(5) [CpFe(CO)2]2
"
(CO)CpFe—FeCp(CO)
CR2
CO
8

Scheme V (cont'd)



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3. This statement is based on the observation that metallocarbenes, in particular the methylene complexes, are very reactive and frequently difficult to isolate. Bridging methylene complexes, on the other hand, appear to be generally amenable to isolation and are stable at room temperature.

4. See for example: Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P.; *Chem. Commun.*, **1978**, 221; (b) Guthrie, D. J. S.; Khand, I. U.; Knox, G. R.; Kollmeier, J.; Paulson, P. L.; Watts, W. E.; *J. Organomet. Chem.*, **1975**, *90*, 93; (c) Garnier, F.; Krausz, P; Dubois, J.-E.; *J. Organomet. Chem.*, **1979**, *170*, 195; (d) Pertici, P.; Vitulli, G.; *Tetrahedron Lett.*, **1979**, 1897.

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