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THE CHEMISTRY OF 1,4-DEHYDROBENZENES

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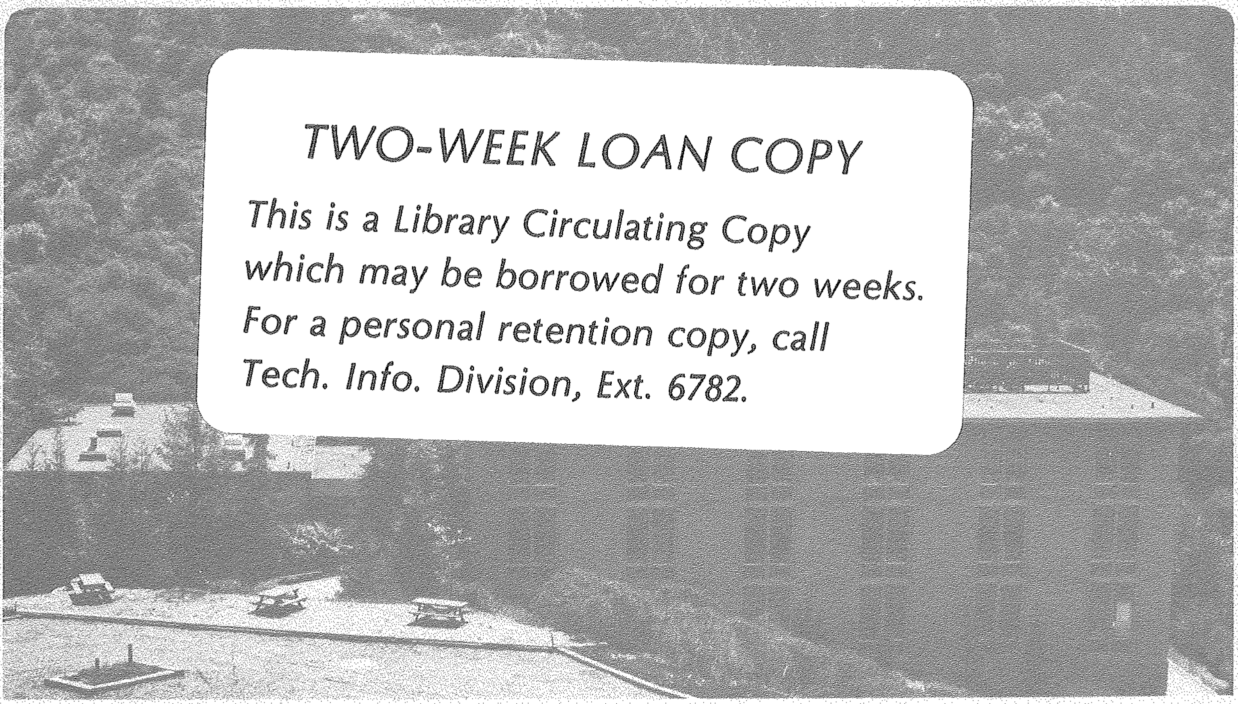
Thomas P. Lockhart
(Ph.D. thesis)

August 1980



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# THE CHEMISTRY OF 1,4-DEHYDROBENZENES

Thesis by

Thomas P. Lockhart

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

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Pasadena, California

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Berkeley, CA 94720

..."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.

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## 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

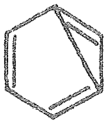
# INTRODUCTION

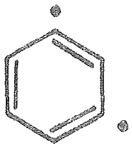
## General

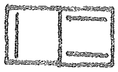
The highly reactive group of isomeric dehydrobenzenes, or benzynes, have provided challenging synthetic, mechanistic and theoretical targets for a number of years.[1] Of particular interest in these molecules is the extent of interaction between the dehydro-centers. The o-benzyne isomer (1) has been 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.

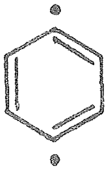
1

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


2b


3a

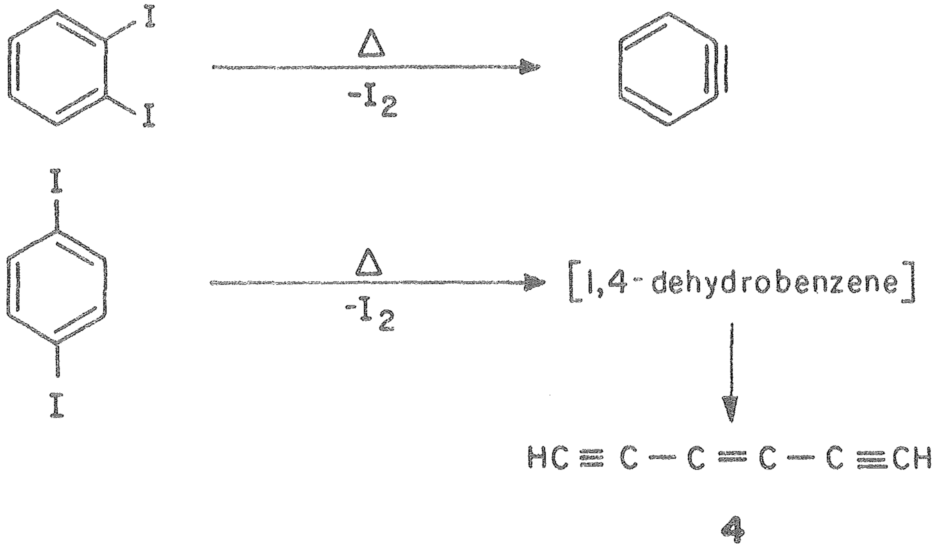

3b

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.

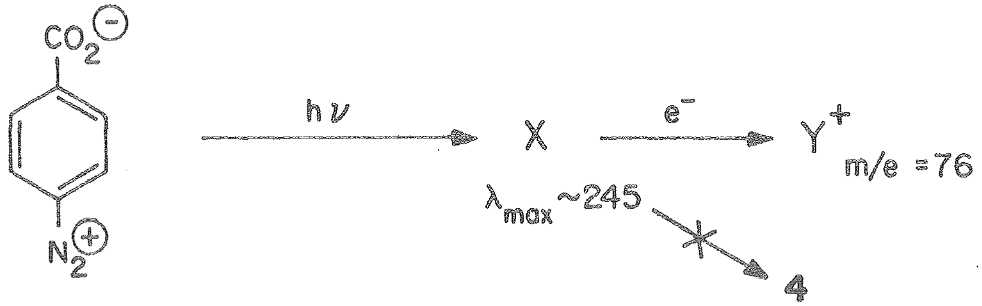
## Literature Survey

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

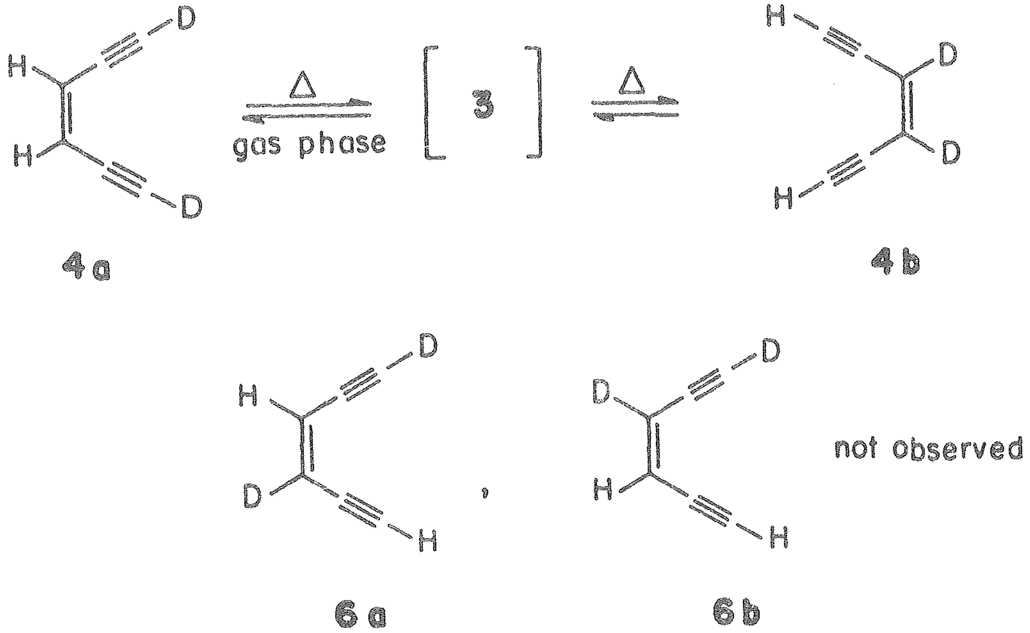


ionization potential of 9.46 eV. From these data they assigned the product of the pyrolysis to diethynyl olefin 4.

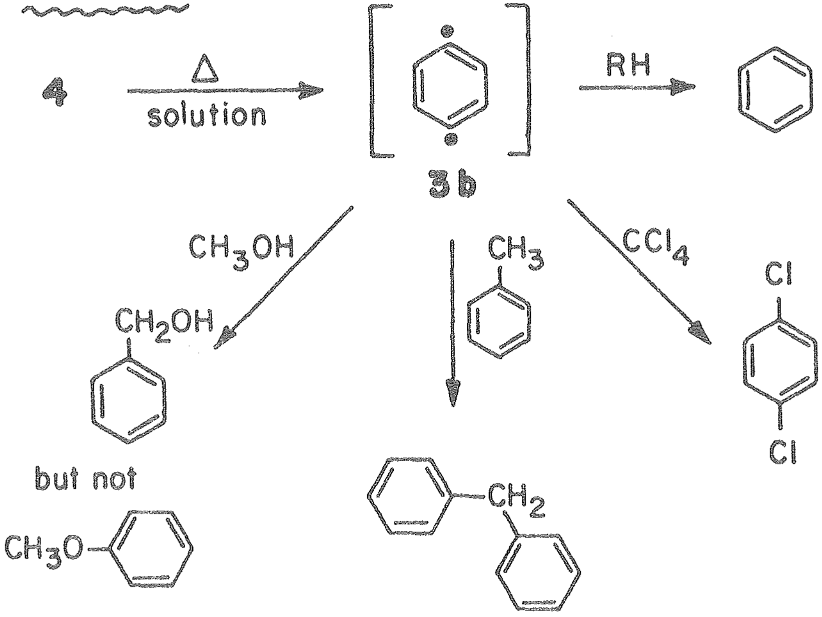
Berry and coworkers[5] attempted to generate 1,4-dehydrobenzene by the photolysis of compound 5 (Scheme II). Monitoring the reaction by flash-absorption optical spectroscopy and time-resolved mass spectroscopy, they observed a signal at m/e 76. From time-of-flight experiments they estimated the lifetime 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

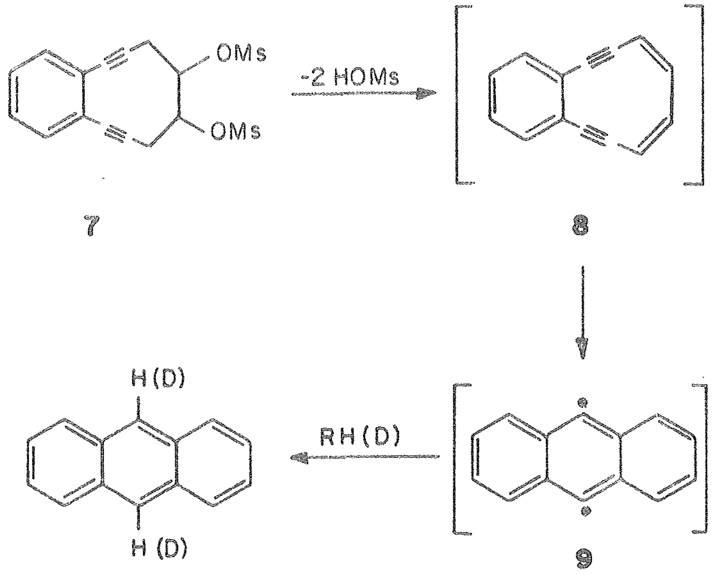


strongly suggested a biradical structure (3b) for at least the reactive form of the intermediate. The trapping observed with methanol argued against a zwitterionic description of 1,4-dehydrobenzene, which would have been expected to produce anisole.

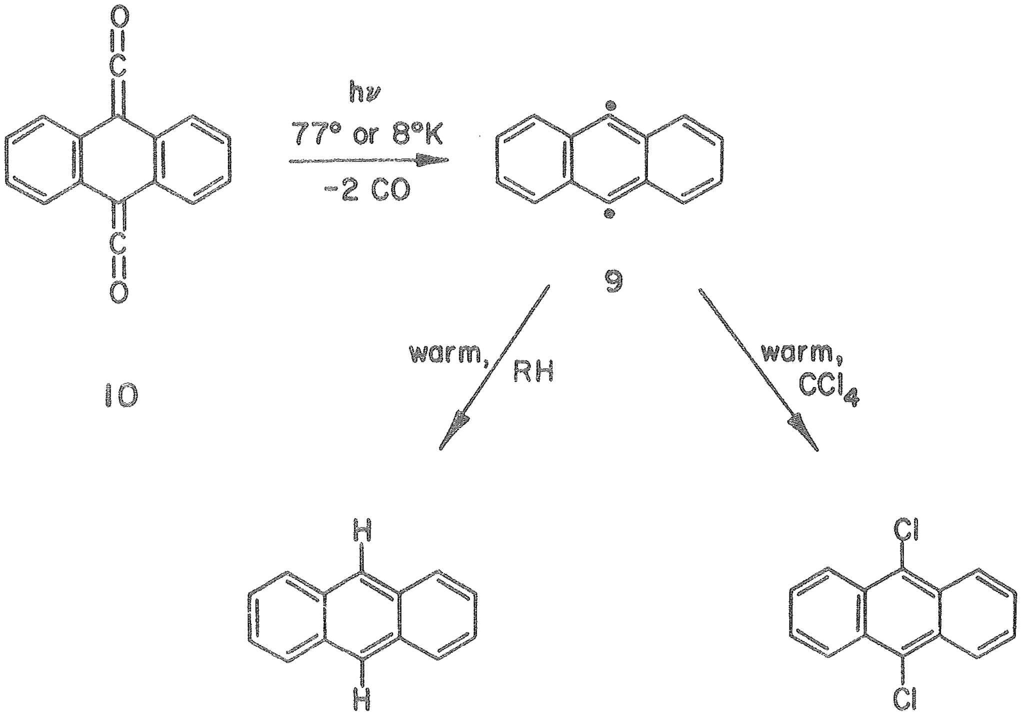
Experiments reported by Chapman and Masamune on related 1,4-dehydroaromatics also provided support for biradical structures. Masamune, et al.[7], performed the elimination of two equivalents of methanesulfonic acid from dimesylate 7 to give 8 (Scheme IV) which contains the elements of a diethynyl olefin 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



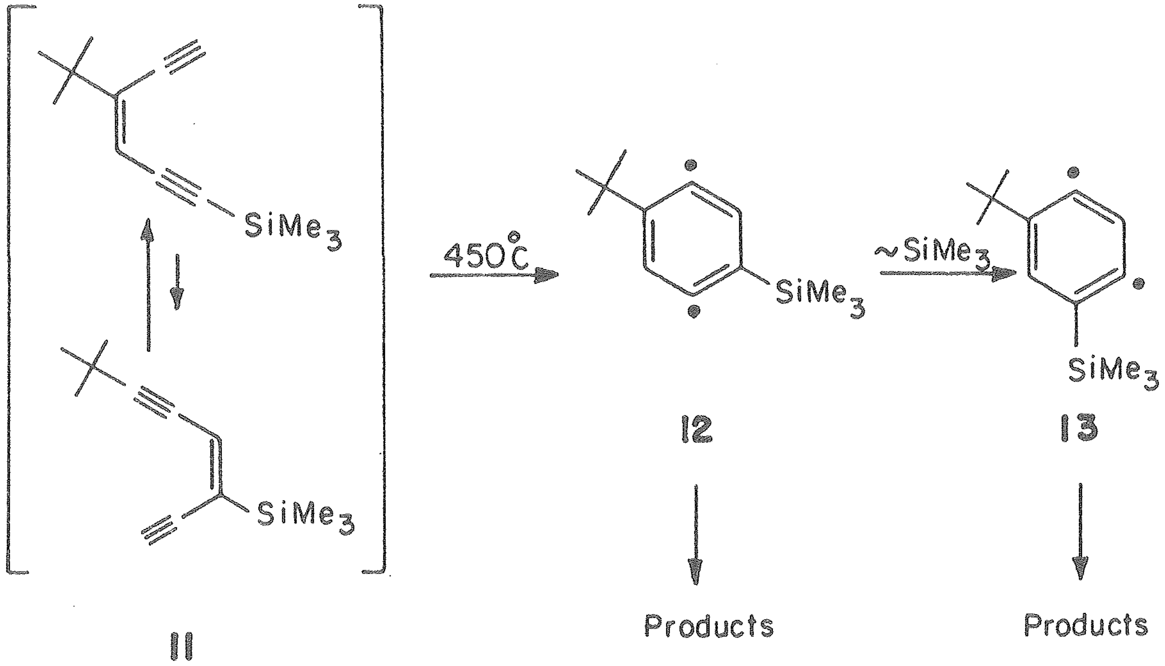
favor of a singlet ground state in 9.

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]

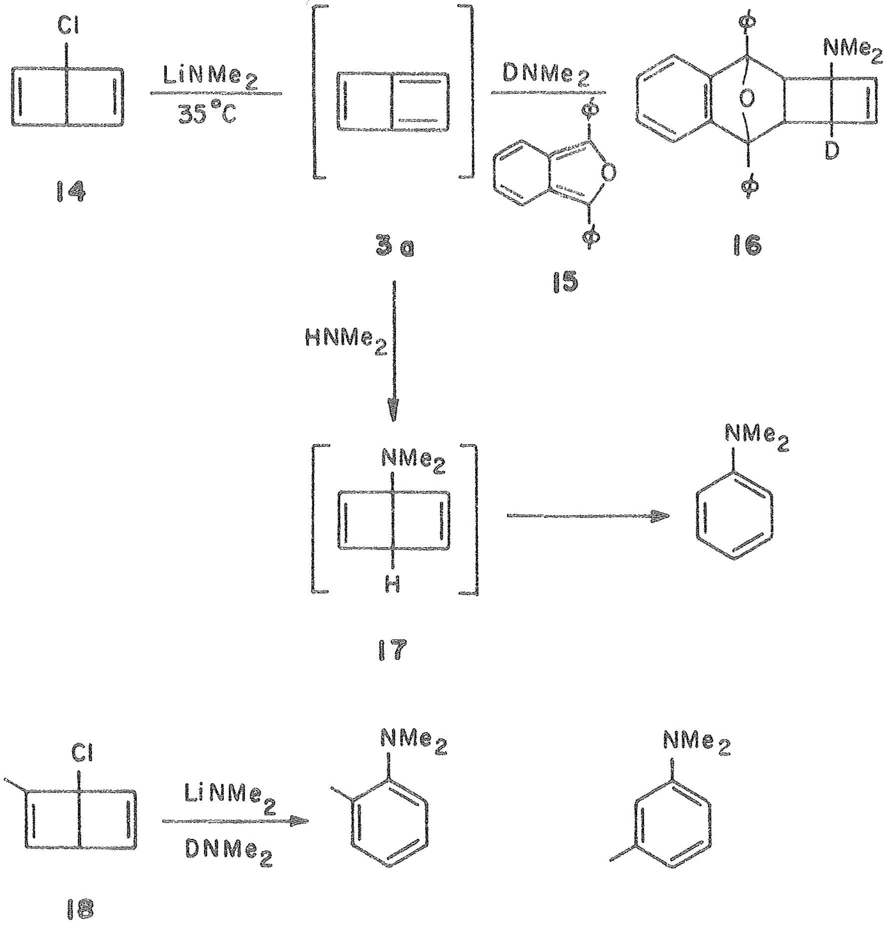
In contrast to the studies cited above, in which the 1,4-dehydroaromatics clearly display biradical reactivity, Breslow, et al.[11], have reported evidence which suggests that they have generated and trapped the bicyclic isomer, butalene (3a). Their approach was to employ a base-induced elimination of 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


SiMe$_3$
SiMe$_3$
450°C
SiMe$_3$
~SiMe$_3$
SiMe$_3$
11
12
13
Products
Products

Scheme VIII

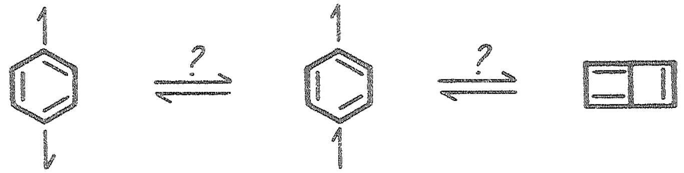


| | | |
|---|---|---|
| relative yield: | 80 % | 20% |
| | % $d_n$ | % $d_n$ |
| $d_0$ | 53 | 21 |
| $d_1$ | 31 | 42 |
| $d_2$ | 14 | 27 |
| $d_3$ | 2 | 9 |

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)<br>SCF-MO-CI | 0 | +3.45 | – |
| Dewar *et al.* (1974)(17)<br>MINDO\|3; lim. CI | +5 | $0(\Delta H_f = +117)$ | +36 |
| Washburn *et al.* (1979)(3a)<br>Ab initio, 4-31G (no CI) | 0 | (+82) | +94 |
| Mueller (1973)(19)<br>Modified MINDO\|2 (no CI) | 0 | (+24) | +18 |
| Noell and Newton (1979)(18)<br>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.

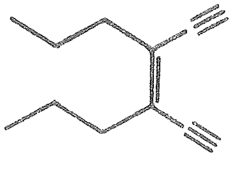
A generalized valence bond (GVB) calculation of the 1,4-dehydrobenzene energy surface was recently reported by Noell and Newton.[18] These authors performed limited geometry optimization for the singlet and triplet states. They concluded that the lowest energy structure of 1,4-dehydrobenzene is the singlet 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]

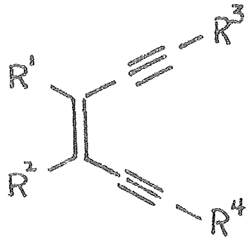

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Table 2. Diethynyl Olefins That Have Been Prepared in this Laboratory.

| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| 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 |

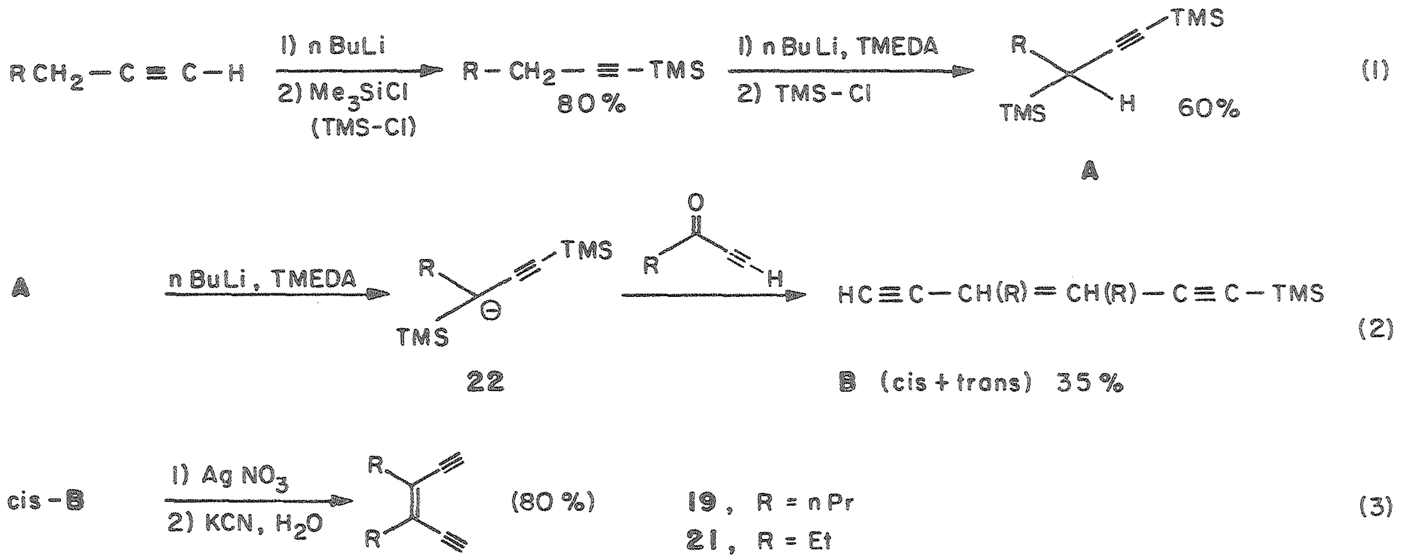
## Results

### Synthesis

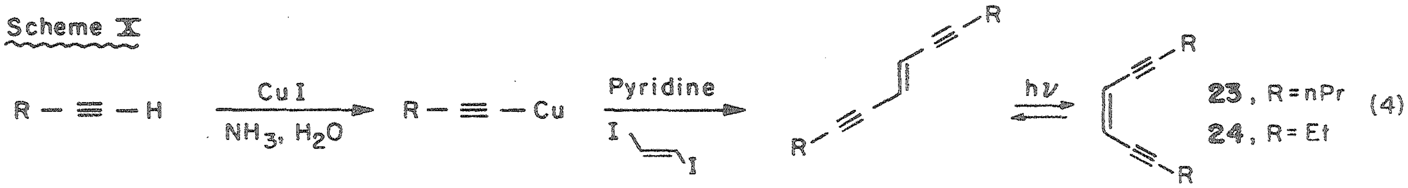
Four diethynyl olefins were prepared in the course of the mechanistic investigations reported in this section. Two contained alkyl substituents at both vinyl positions (19, 21). The synthetic route to these compounds followed a general method previously employed by Gilbert Johnson and John Stofko in 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



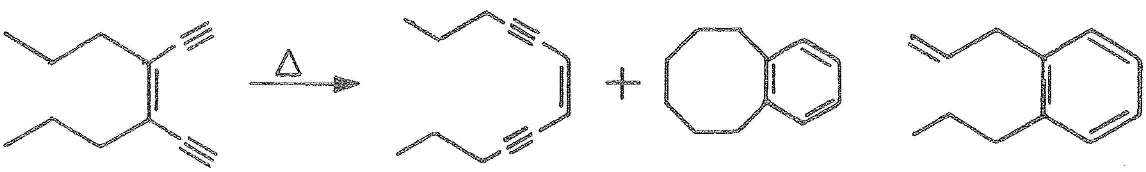
Although the diethynyl olefins obtained after chromatography on silica gel were >95% pure, before pyrolysis they were usually further purified by preparative gas chromatography. This method provided the diacetylenes in >99% purity. The neat diacetylenes could be handled briefly at room temperature in 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

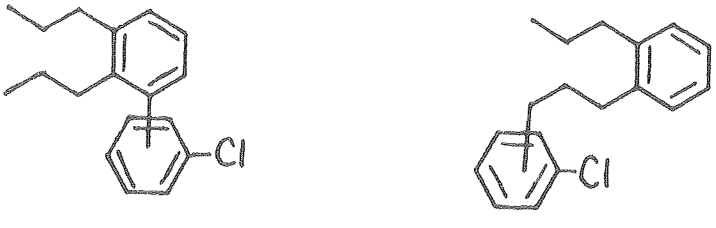
Gas phase experiments were performed by passing the diacetylenes through a heated quartz tube either under a stream of $N_2$ (1 atm pressure) or at reduced pressure. The products were collected on a cold finger at -196° C. Solution reactions were carried out in sealed glass tubes. The concentration of 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



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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%

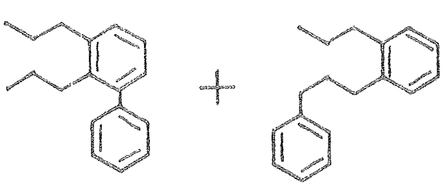
Table 3. Product Yields and Rate Constants in the Solution Pyrolysis of **19**.[a]

| | | | | Absolute Yield (%)[b] | | | | |
|---|---|---|---|---|---|---|---|---|
| Run | T (°C) | $k_{obs}$ (sec$^{-1}$) | 1,4-cyclohexadiene (M) | 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 | $1.3 \times 10^{-3}$ | 0.0 | 13.5 | 38.5 | 20.0 | -- | 72 |
| (5) | 156 | $6.9 \times 10^{-4}$ | 0.0 | 11.8 | 35.8 | 17.2 | -- | 65 |
| (6) | 145 | $2.9 \times 10^{-4}$ | 0.0 | 9.8 | 37.3 | 17.6 | -- | 65 |
| (7) | 132 | $9.3 \times 10^{-5}$ | 0.0 | 7.9 | 38.5 | 16.4 | -- | 63 |
| (8) | 156 | $7.1 \times 10^{-4}$ | 0.19 | 8.7 | 13.5 | 8.7 | 27.6 | 58 |
| (9) | 156 | $6.4 \times 10^{-4}$ | 0.38 | 5.2 | 6.7 | 3.1 | 47.4 | 62 |

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

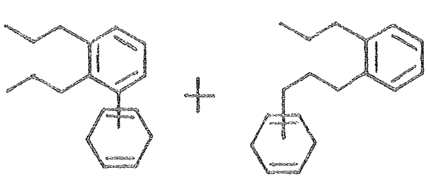
[b] Yields determined by digital integration of FID vpc trace and reference to an internal standard.

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

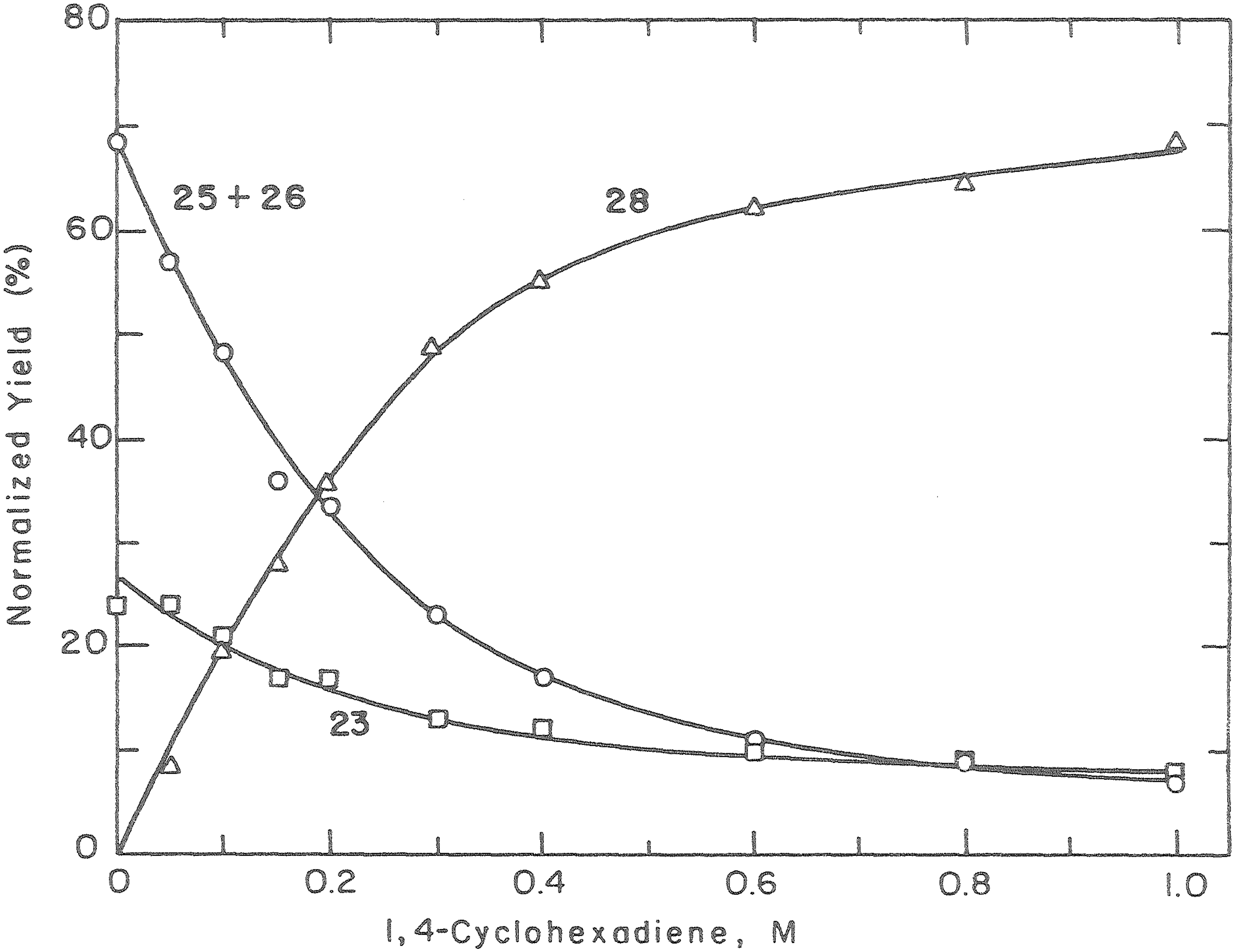


Figure 1. Plot of normalized product yields as a function of the amount of 1,4-cyclohexadiene in the reaction solution.

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.

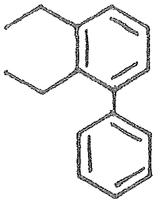
| | | | Absolute Yield (%)[a] | | | | | |
|---|---|---|---|---|---|---|---|---|
| Run | Phase | T(°C) | 24 (c + t) | styrene | benzocyclobutane | o-allyl styrene | tetralin | o-diethyl benzene |
| (1) | gas[b] | 400 | 100 | 0 | 0 | 0 | 0 | 0 |
| (2) | gas[b] | 500 | 76.8 | 1.3 | 7.8 | 8.8 | 1.6 | 0 |
| (3) | benzene solution[c] | 195 | 51 | 0 | 0 | 0 | 0 | 5 |
| (4) | benzene + 1,4-cyclohexadiene (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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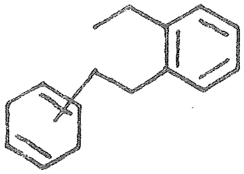

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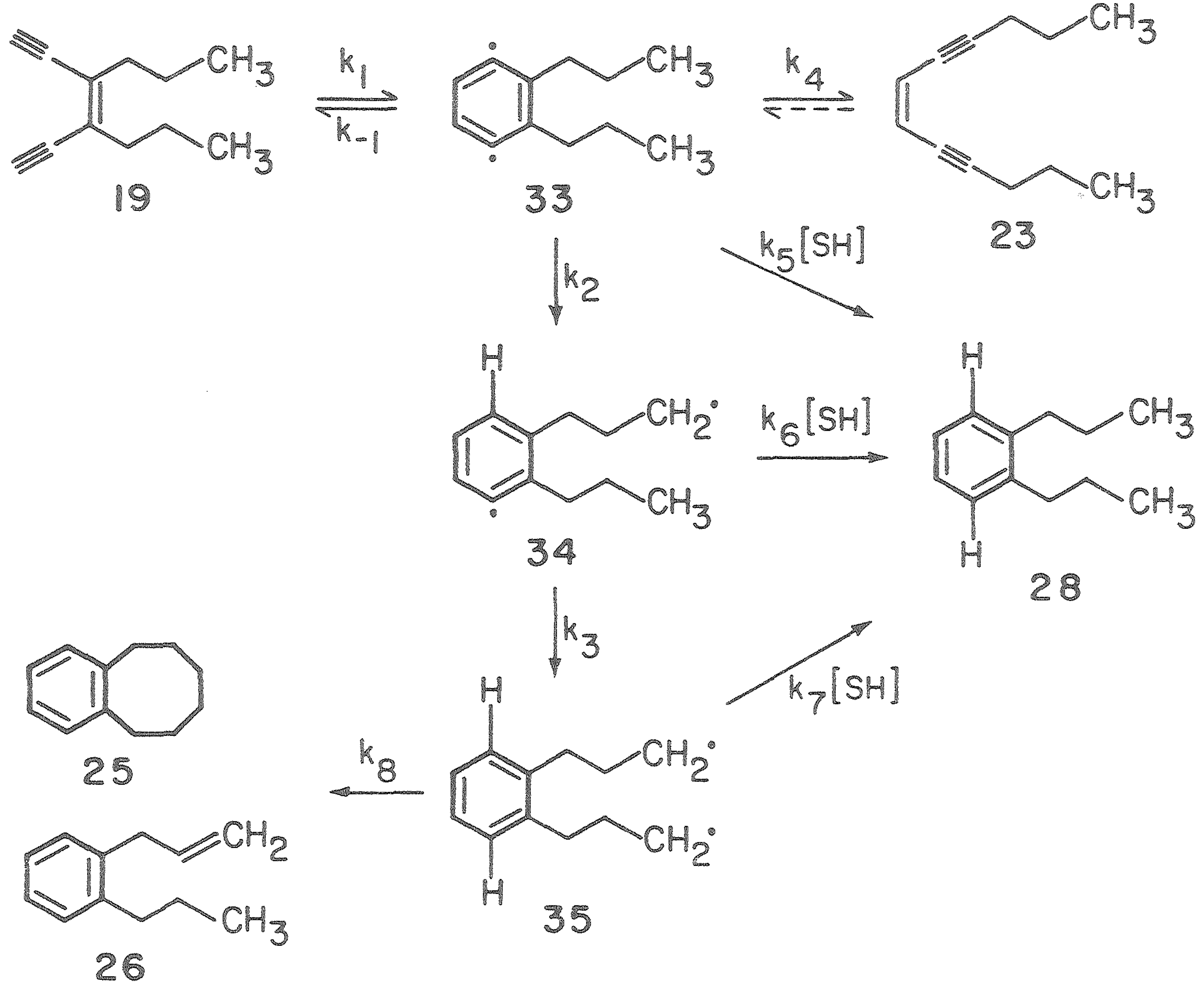
# Discussion

## 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° 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

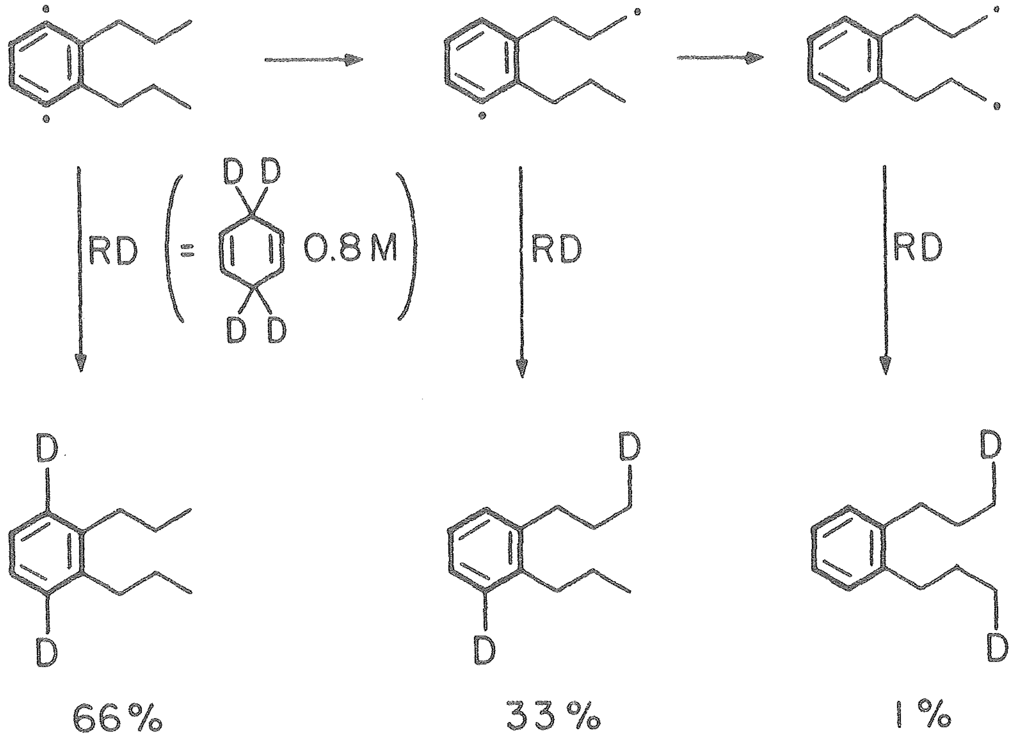


benzocycles or o-propyl-β-methylstyrene argues against the occurrence of other intramolecular hydrogen transfer modes (ie. [1,4]) in 33 or 34.

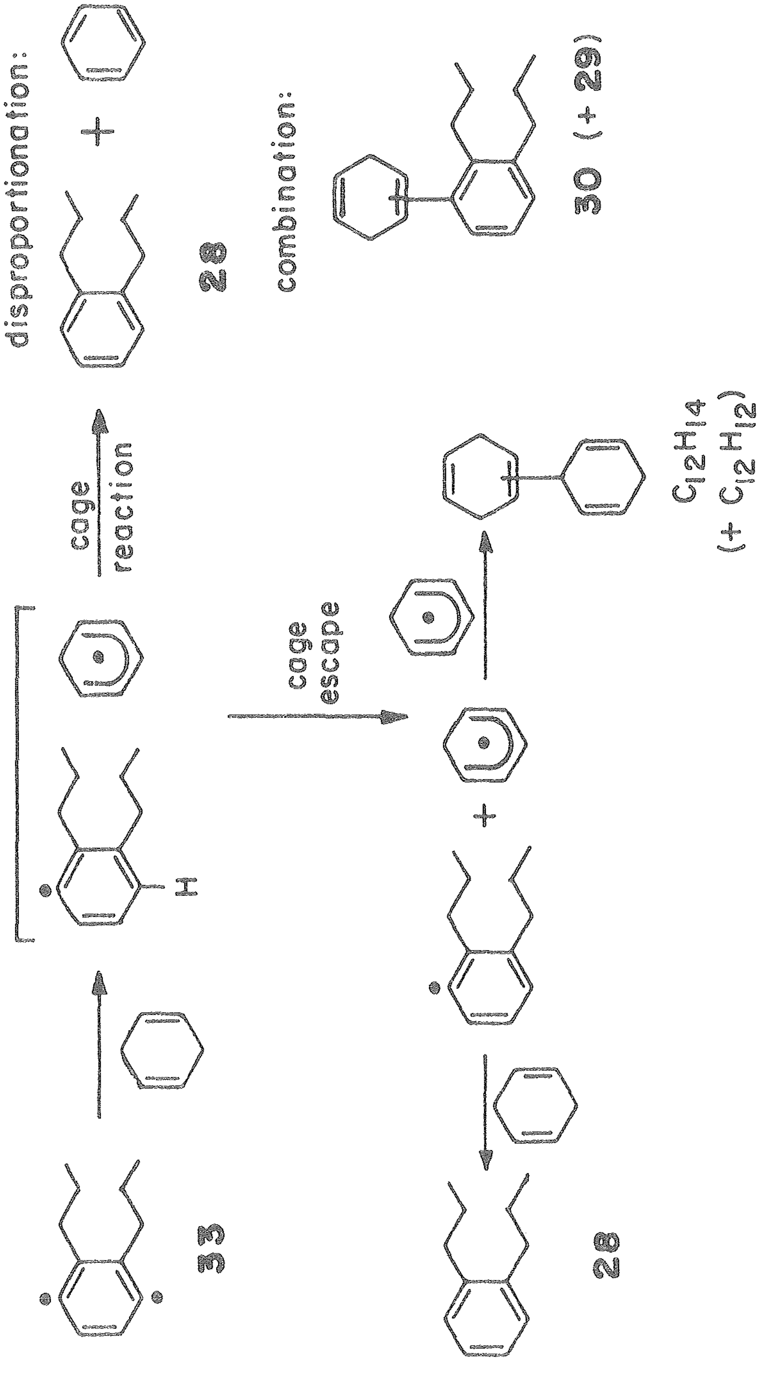
The presence of 1,4-cyclohexadiene in the reaction solution leads to the formation of 28 which may in principle come from trapping of any of the three biradical intermediates. The results of the deuterium labelling study mentioned previously (see the Results section) indicate that trapping occurs predominantly 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

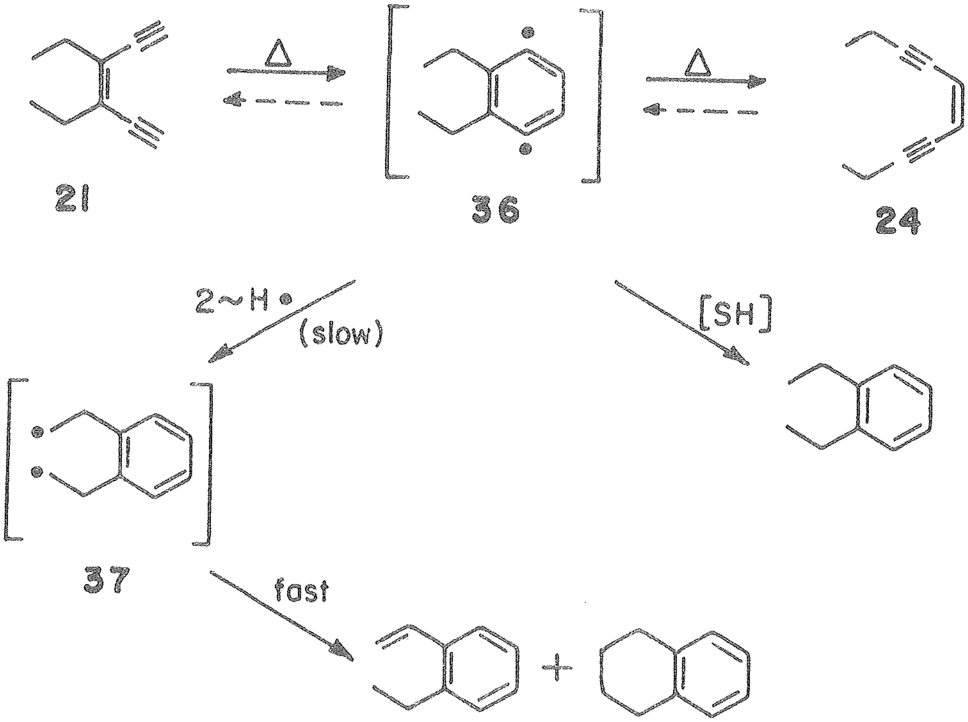

33
28
cage reaction
disproportionation:
28
combination:
30 (+ 29)
cage escape
$C_{12}H_{14}$
$(+ C_{12}H_{12})$
28

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 (_ca_. 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 $\log_{10}A = 10.8 \pm 0.3\ \mathrm{sec}^{-1}$).

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

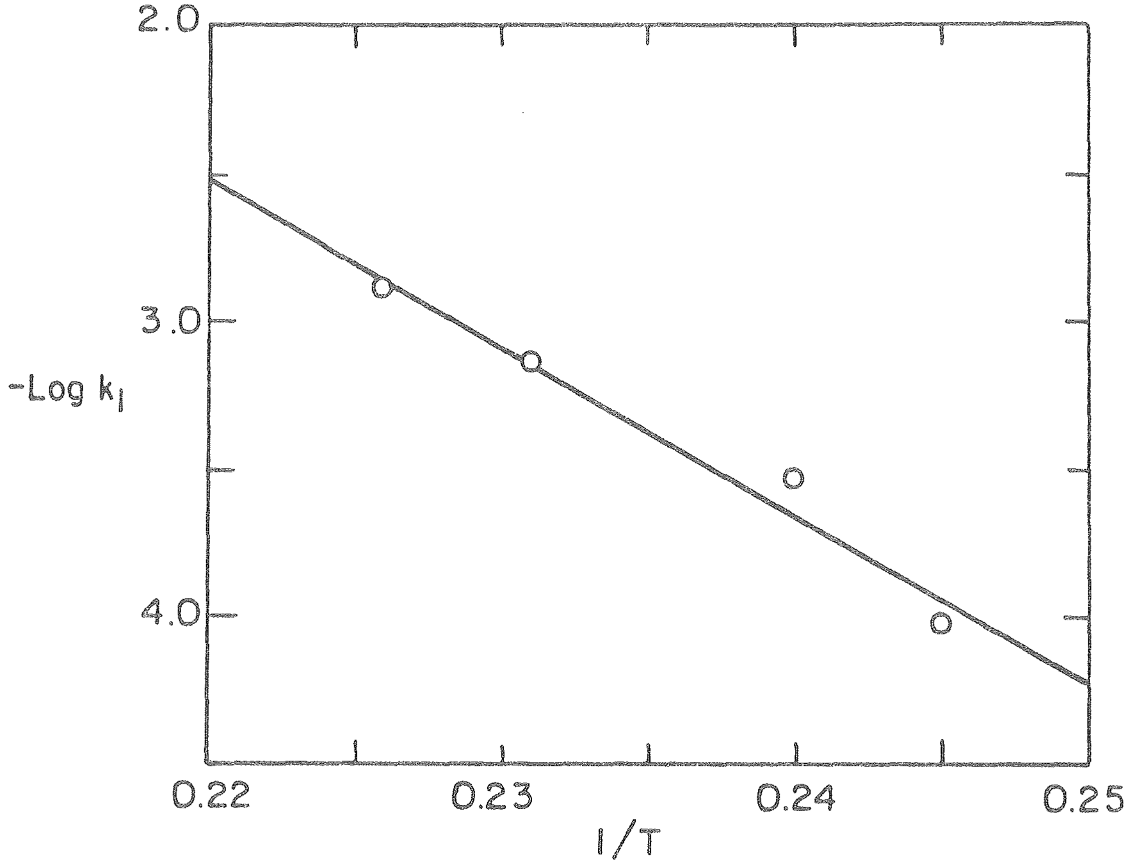


Figure 2. Arrhenius plot of unimolecular rate constants observed in the reaction of 19 (0.01 M) in chlorobenzene.

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.

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

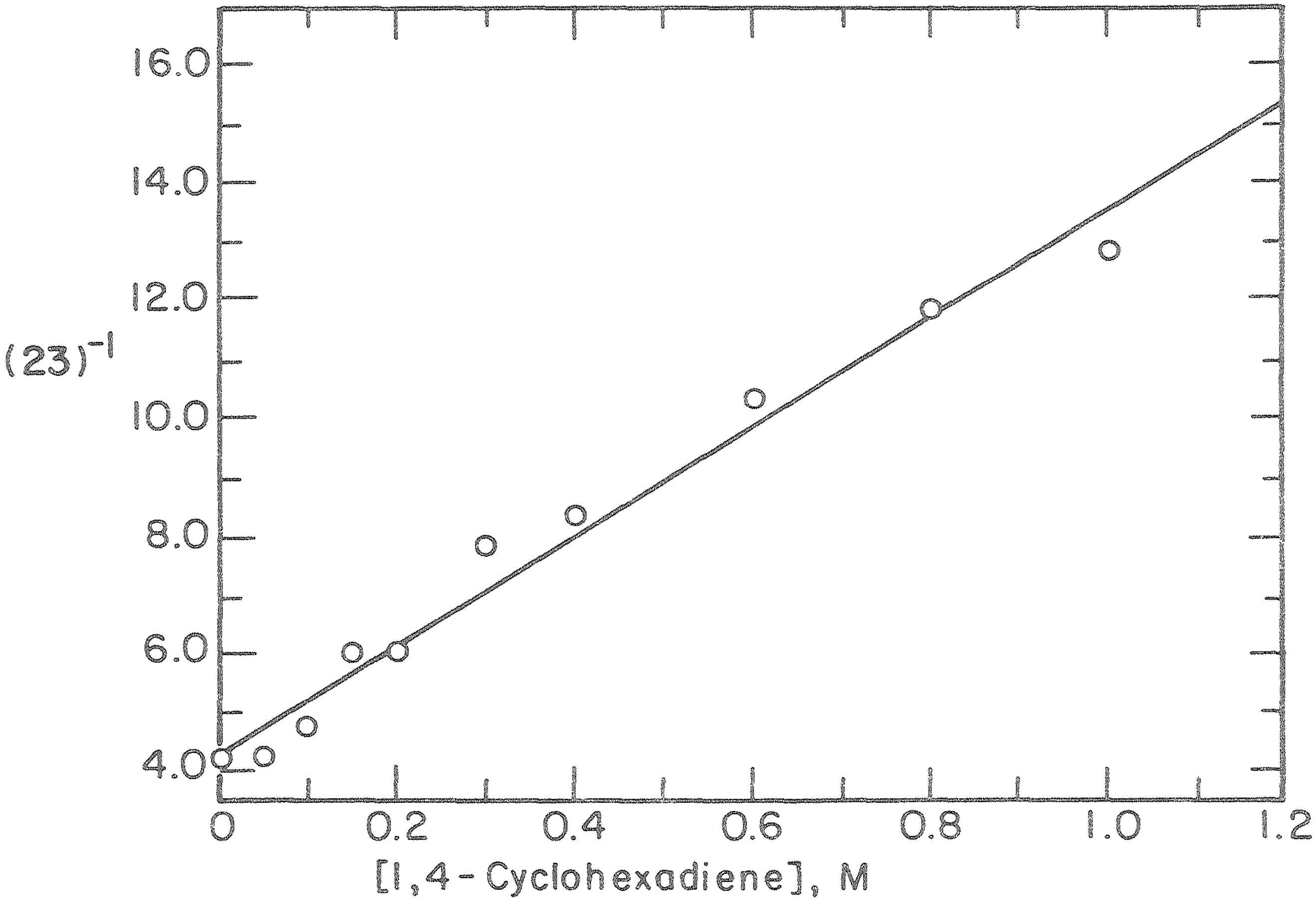


Figure 3. Plot of (normalized yield of 23)$^{-1}$ versus concentration of 1,4-cyclohexadiene. Conc. 19 = 0.01 M, T = 190° C.

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**.

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

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

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 $0.36 \pm 0.01$; 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

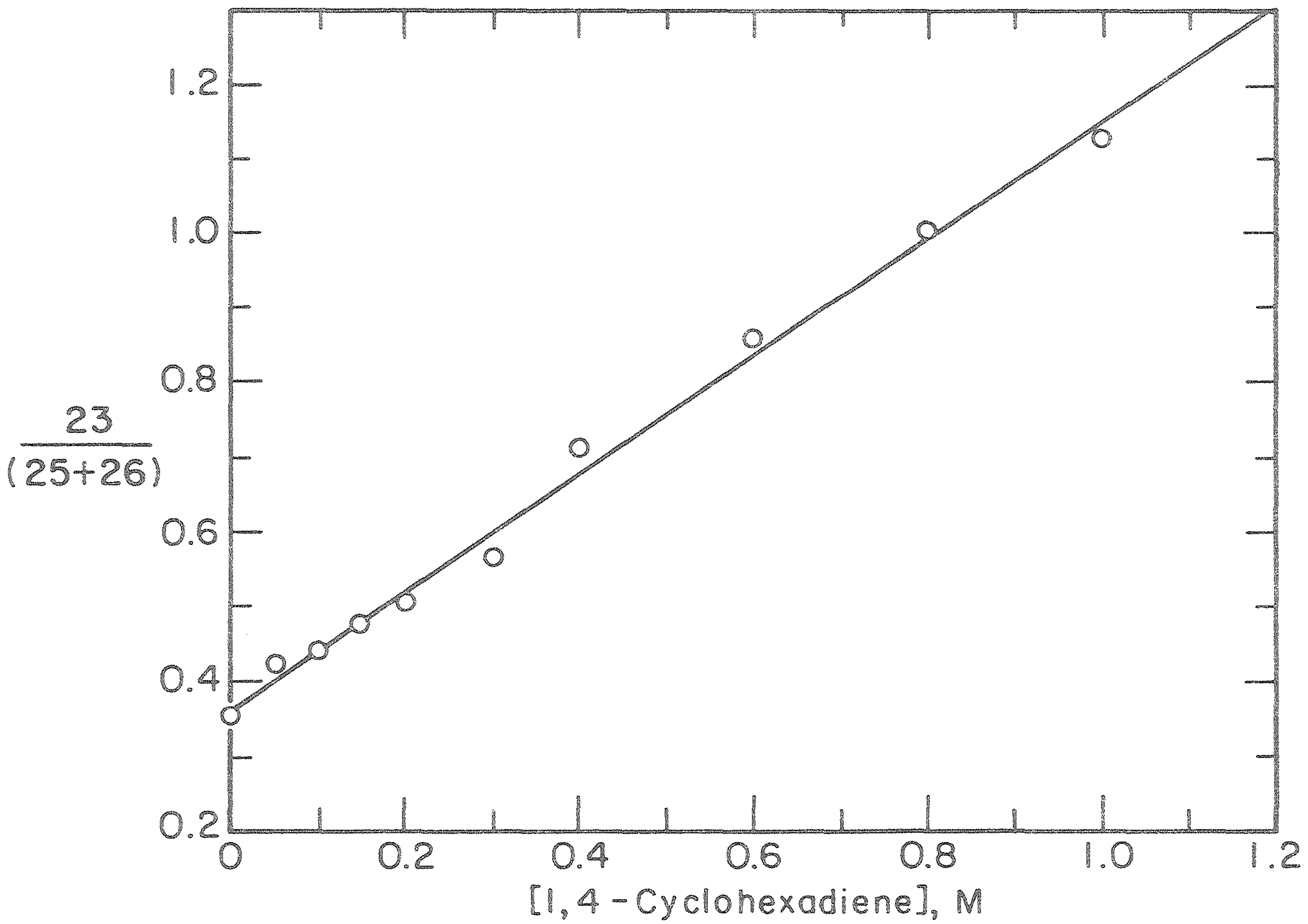


Figure 4. Plot of the ratio of the observed yields of 23/(25 + 26) as a function of 1,4-cyclohexadiene concentration. Concentration of 19 = 0.01 M, T = 190° C.

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 $160^{\circ}$ 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

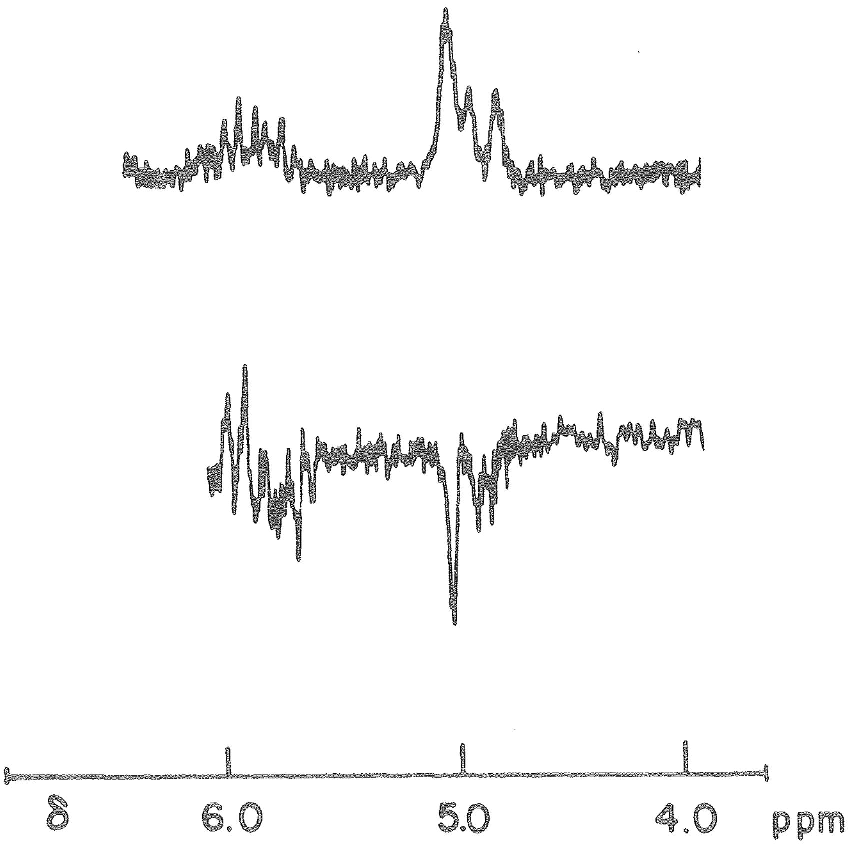


Figure 5. The upper spectrum (90 MHz $^1H$) shows the vinyl region of a purified sample of o-allyl-n-propylbenzene recorded at 30° C. The lower spectrum shows the emissive signals observed during reaction of **19** at 160° C in a 90 MHz NMR probe. The signals appearing in absorption on the left side 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 $7.7 \times 10^6$ $M^{-1}$ $sec^{-1}$ at $60^\circ$ 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 $60^\circ$ 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 $64^\circ$ 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 $5.2 \pm 0.4$ 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

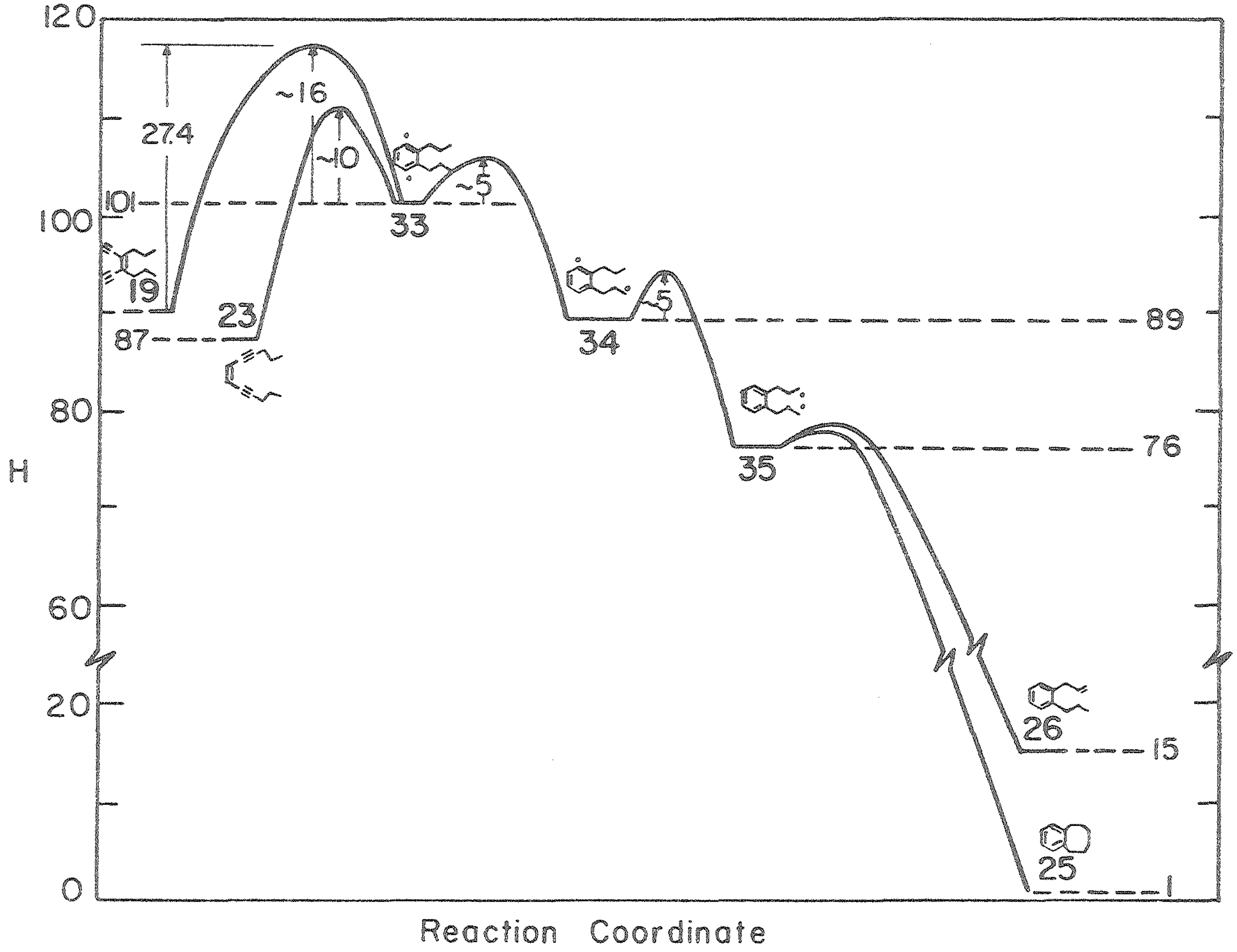


Figure 6. Enthalpy diagram for the reaction of 19 (all units in kcal/mole).

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 ($CDCl_3$): $\delta$ 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 ($CDCl_3$): $\delta$ 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). $^1H$-NMR ($CDCl_3$): $\delta$ 0.09 (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: $^1H$-NMR ($CDCl_3$): $\delta$ 0.10 (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-bis(trimethylsilyl)hexyne (3.0 g, 13 mmol). With rapid magnetic stirring at $-20^{\circ}$ 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 $-70^{\circ}$ 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 ($DCCl_3$): $\delta$ 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$^{-1}$. Anal. 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 ($CDCl_3$): $\delta$ 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$^{-1}$. Anal. 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 ($CDCl_3$): $\delta$ 0.21 (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 ($CDCl_3$): $\delta$ 0.21 (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 ($CDCl_3$): $\delta$ 0.80 (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 ($CDCl_3$): $\delta$ 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 ($CDCl_3$): $\delta$ 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$^{-1}$. Anal. 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 ($CCl_4$): $\delta$1.13 (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: $^1$H-NMR ($CDCl_3$): $\delta$1.04 (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: $^1$H-NMR ($CCl_4$): $\delta$1.19 (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 $^1H$-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° 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 $3 \times 10^{-2}$ 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 ($CCl_4$): $\delta$ 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 ($CCl_4$): $\delta$ 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 ($CCl_4$): $\delta$ 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° 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° 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° 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° C for 15 min, temperature program = 6°/min, final temperature = 200°) 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° C). At the concentrations employed, reduction to yield o-dipropylbenzene occurred to the extent of *ca.* 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

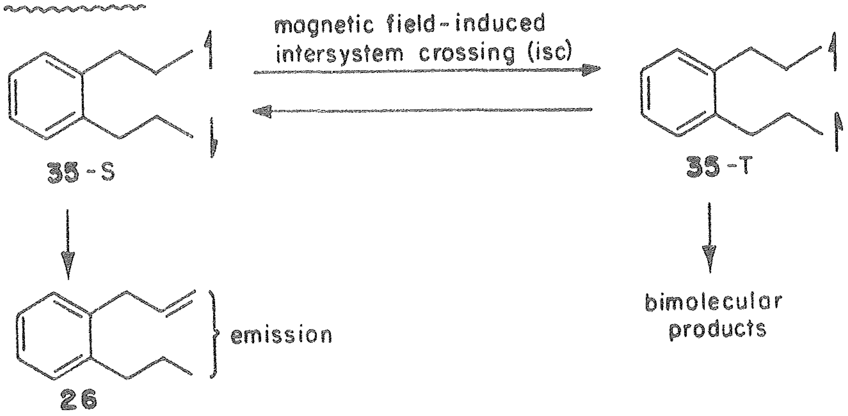
## Introduction

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-$T_o$ 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

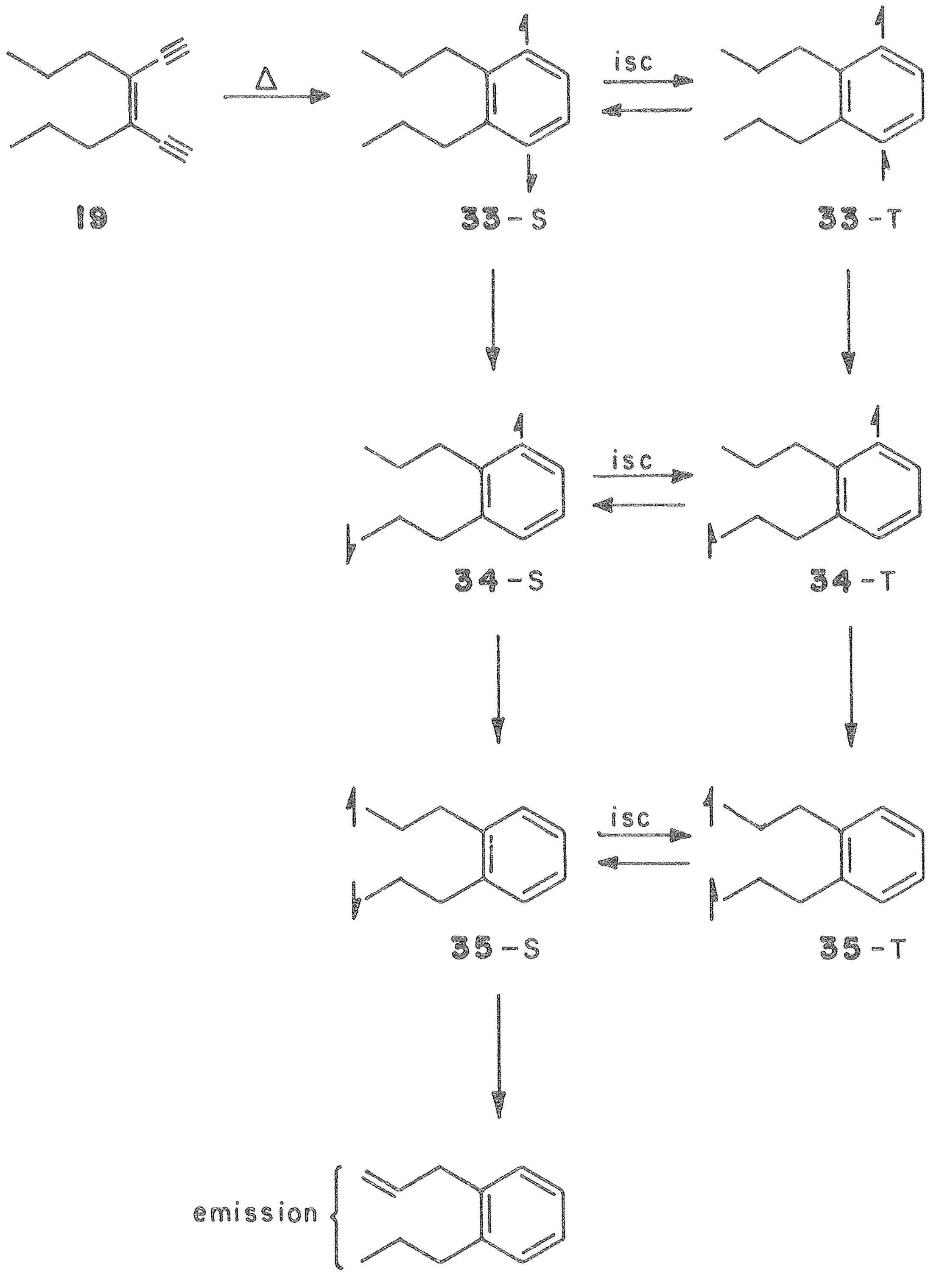


## Results and Discussion

### 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.

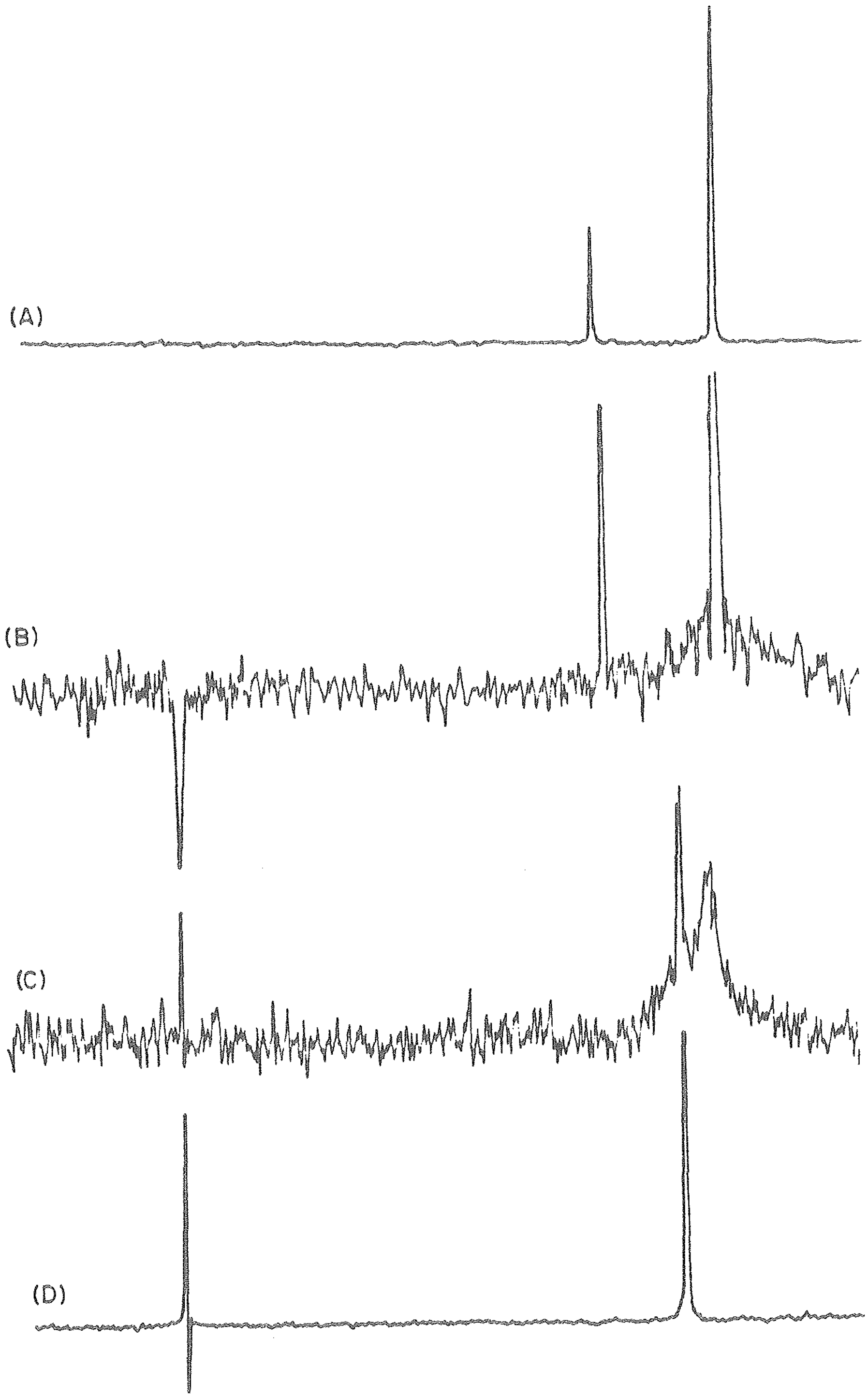
Thermal reaction of dilute solutions of **38** (0.01 M) in hexachloroacetone and $CCl_4$ gave results (Table 5) similar to the NMR experiment. Product **39** was isolated from a $CCl_4$ solution reaction by preparative VPC and characterized by IR, $^1$H-NMR and HRMS.

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-



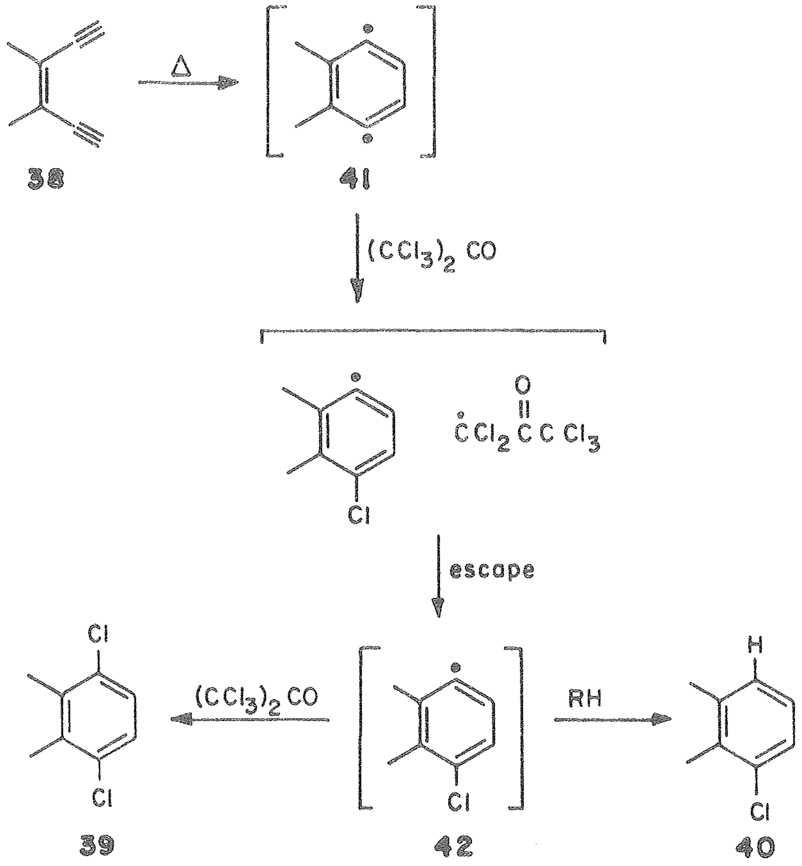
<u>Figure 7.</u> CIDNP observed during reaction of a hexachloroacetone solution of 38. (A) NMR of solution before reaction. (B) Signals observed during reaction at 160° C. (C) Room temperature spectrum after complete reaction of 38. (D) Spectrum of 39 in $CCl_4$.

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 $\epsilon$ 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 $\Delta g = (-)$. The hyperfine coupling constant in phenyl radicals is positive for the ortho, meta and para hydrogens, so $A_i = (+)$. The remaining parameter, $\mu$, 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 $\mu$, 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



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

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

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

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

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

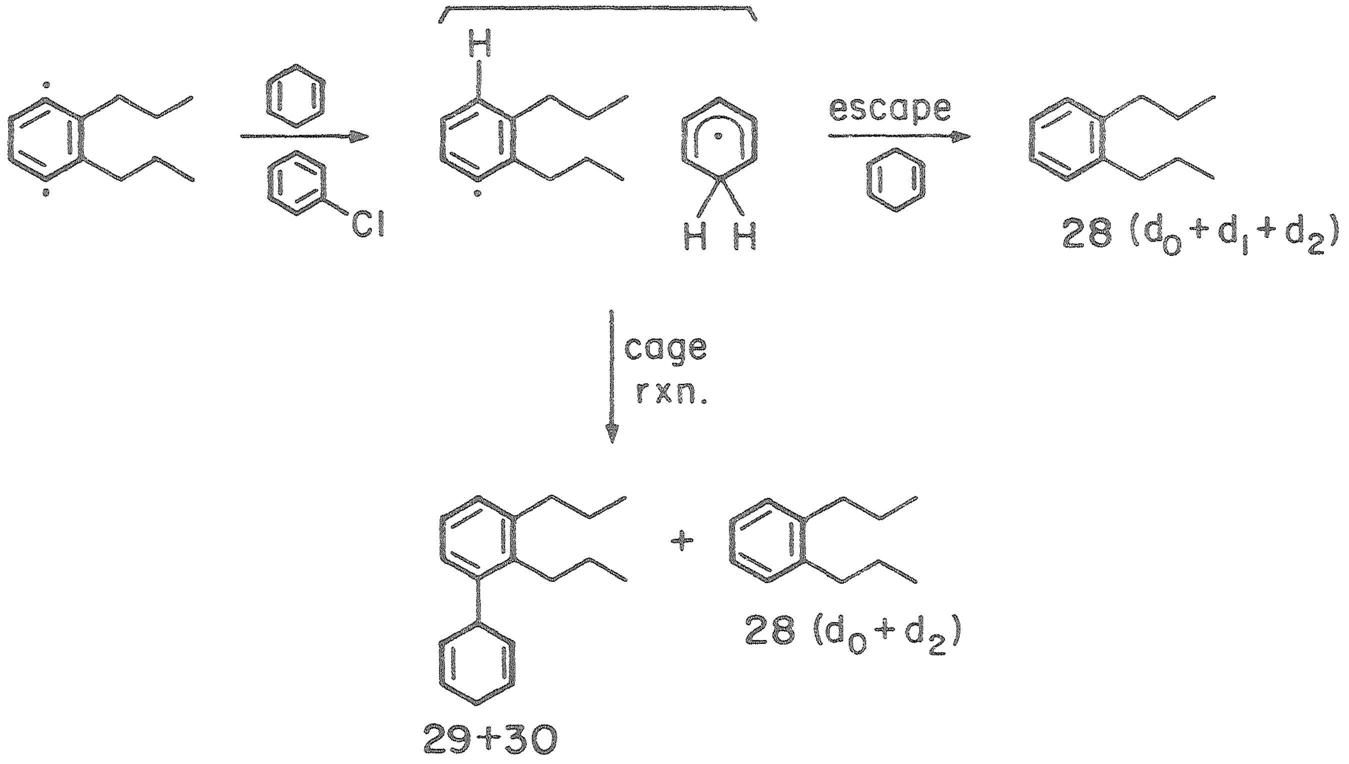
$A_i$ $\begin{cases} + \\ - \end{cases}$ sign of hyperfine coupling constant arose from singlet 35 or that triplet 35 was produced as a result of intersystem crossing in biradical 34 or 35 but not in the 1,4-dehydrobenzene biradical.

## 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

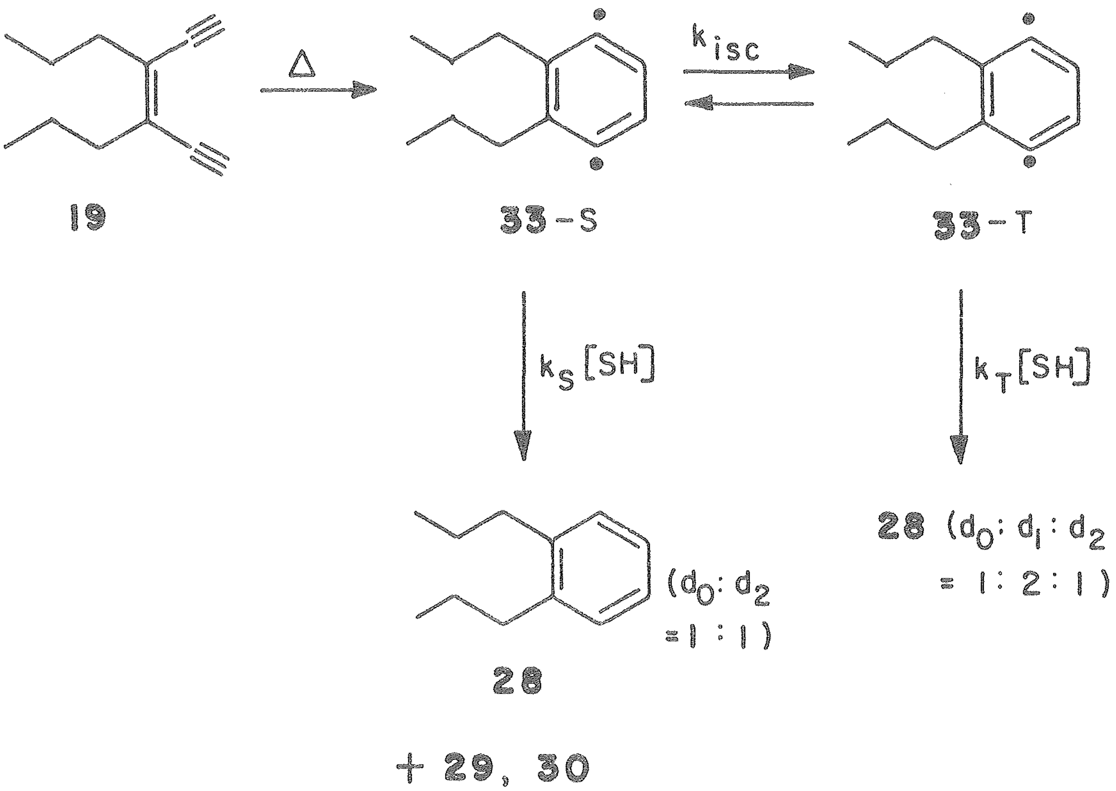
Scheme XIX



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-$d_o$ and -$d_4$ is used in the reaction solution. Consider first the reaction of **33** with cyclohexadiene-$d_o$. 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**-$d_o$ 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**-$d_o$ 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**-$d_o$ and -$d_2$ (1:1 ratio) and escape reactions of the radical pair should give **28**-$d_o$, -$d_1$ 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**-$d_o$, -$d_1$ 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

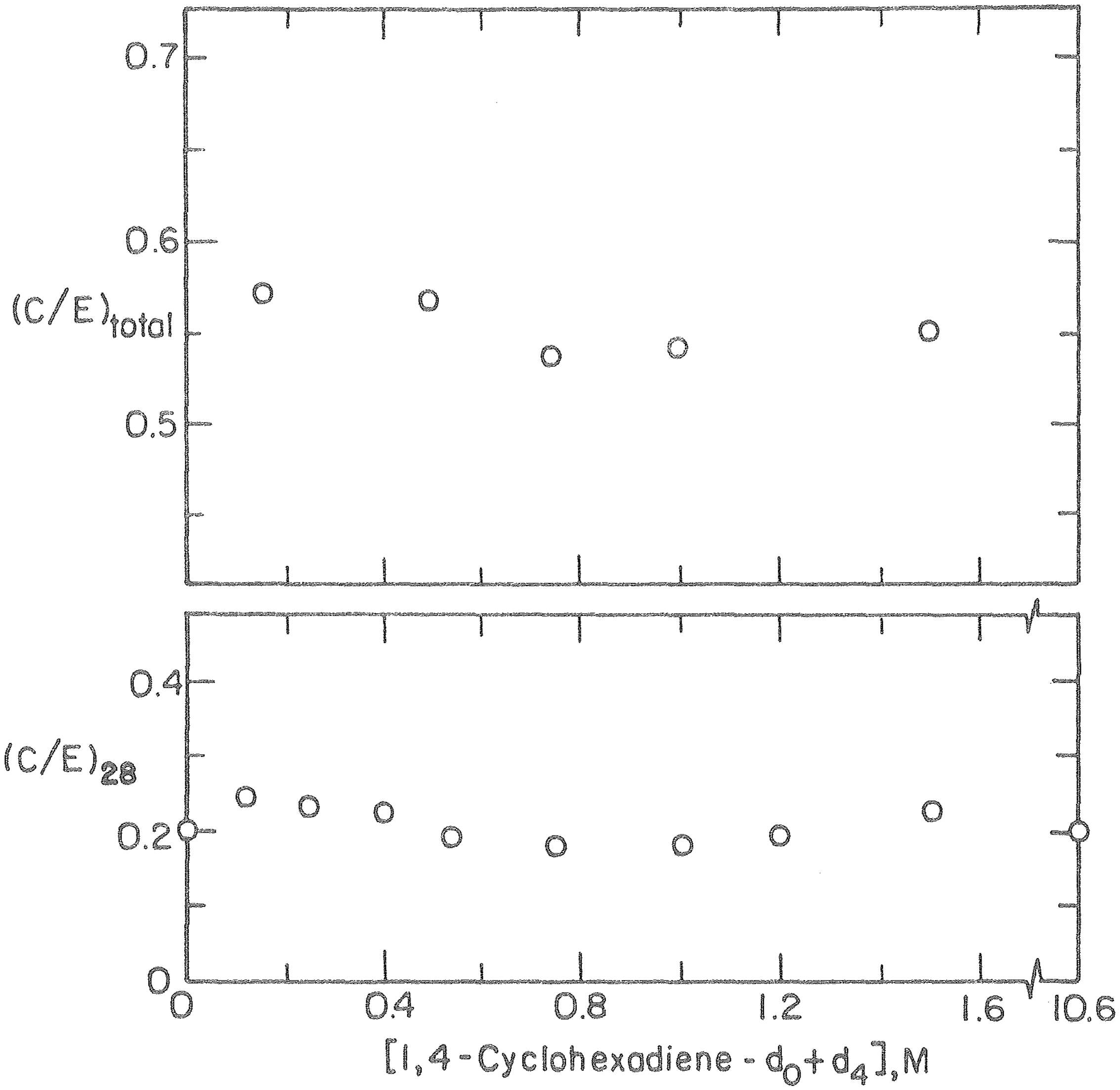


Figure 8. Ratio of C/E observed in the reaction of 19 (0.01 M, 195° C) as a function of 1,4-cyclohexadiene concentration. Upper plot shows C/E for products 28, 29 and 30. Lower plot shows C/E for product 28 alone.

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

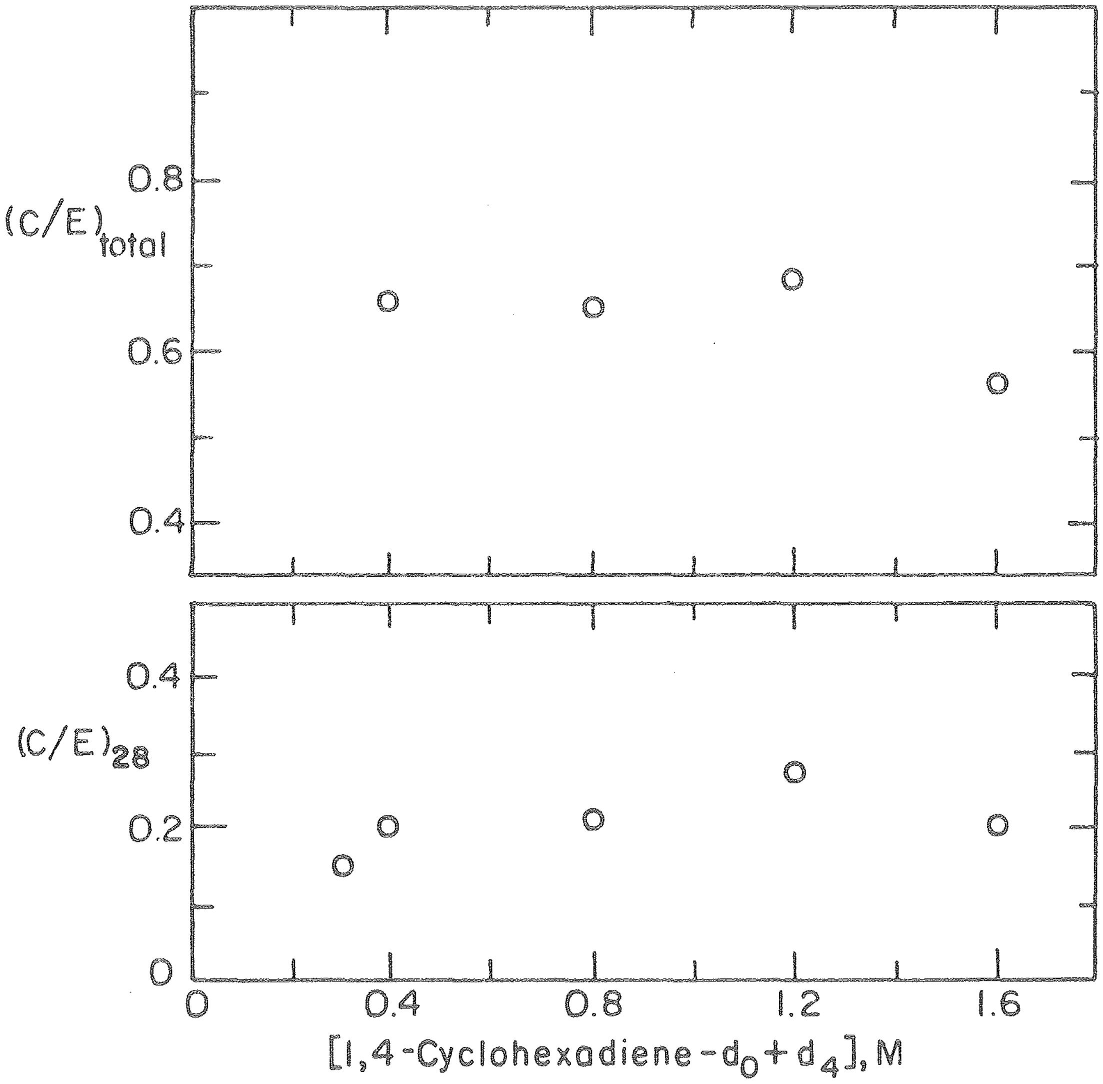


Figure 9. Ratio of C/E observed in the reaction of 19 (0.01M, 195° C) in bromobenzene solution as a function of added 1,4-cyclohexadiene. Upper plot shows C/E for products 28, 29, and 30. Lower plot shows C/E for product 28 alone.

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 $200^\circ$ 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 ($CCl_4$): $\delta$ 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 ($CDCl_3$): $\delta$1.88 (s,6H), 3.17 (s,2H). IR (thin film): 3310, 3020, 2935, 2874, 2108, 1445, 1386, 1250, 1156, 1103 cm$^{-1}$. Trans isomer: NMR ($CDCl_3$): $\delta$2.02 (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 cis 38, 104.0623; found for trans 38, 104.0622.

## Thermal Reactions

**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 (eg. 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 ($CCl_4$): $\delta$ 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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