July 29, 1975

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I am submitting herewith a dissertation written by Charles R. Watson, Jr. entitled "1,8-Naphthoquinodimethane." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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1,8-NAPHTHOQUINODIMETHANE

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee

Charles R. Watson, Jr.

August 1975

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Ms. Sandra T. Watson is due the author's most sincere appreciation for her perseverance.

ABSTRACT

The successful preparation and characterization of a bridged 1,8-naphthoquinodimethane is reported. The azo precursor was prepared via the Diels-Alder adduct of pleiadiene and diethyl azodicarboxylate. The adduct was hydrogenated, hydrolyzed and oxidized to give the desired azo compound. Attempts to synthesize pleiadiene via the reaction of phenalenone with dimethyloxosulfonium methylide were unsuccessful. Reaction of the phenalenyl anion with methylene chloride and n-butyl lithium gave pleiadiene as a minor product and naphtho [1',8'] tricyclo [4.0.0] hept-2-ene Knoxvalene, as the major product. Several methods were found to convert Knoxvalene into pleiadiene. Both pyrolysis and photolysis of the azo compound in a variety of solvents afforded 1,8-naphthocyclobutane (major product) and 1,8-divinylnaphthalene (minor product); no other products were formed. The product ratio, 1,8-naphthocyclobutane/1,8-divinylnaphthalene, was not altered when singlet-triplet perturbing agents such as air, iodobenzene, and hexafluorobenzene were added. Attempts to trap the bridged 1,8-naphthoquinodimethane using olefins were unsuccessful. Both pyrolysis and photolysis of stereospecifically labelled azo precursor gave 1,8-naphthocyclobutane and 1,8-divinylnaphthalene with a "random" deuterium distribution. This result demonstrates the existence of the bridged 1,8-naphthoquinodimethane. When a sample of the azo compound in hexafluorobenzene was irradiated in an esr cavity, the spectrum of a thermally accessible triplet sate of

bridged 1,8-naphthoquinodimethane was observed. INDO calculations suggest that the observed triplet has either a bent or twist conformation while the ground state singlet has a twist conformation. A coherent mechanism which explains the results is presented.

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CHAPTER I

INTRODUCTION

The purpose of this chapter is to provide background material necessary for the interpretation and understanding of the discussion of 1,8-naphthoquinodimethane presented in Chapter II. In order to achieve this goal, this chapter will cover several major related areas. The first section will deal with diradicals from both a theoretical and a practical point of view. This will be followed by sections dealing with ground state triplets and high spin systems. A fourth section will then be presented which describes the various aspects of cyclic azo compounds including synthesis, mechanisms of decomposition, and overall utility as a synthetic tool. The final section will be a summary of the current knowledge of quinodimethanes as a molecular category.

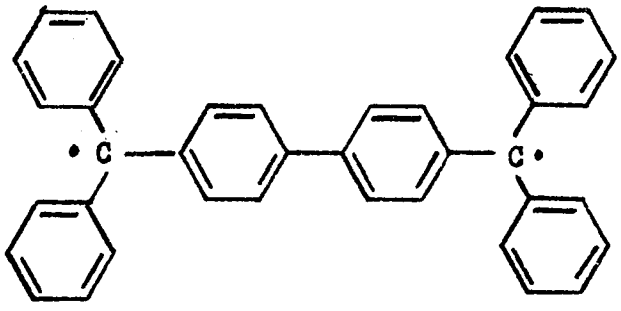
A. Diradicals

This section serves to define electron spin and to illustrate its ramifications. Following this definition the commonly held definitions of diradicals will be presented and their characteristics examined. In concluding this section an attempt will be made to treat diradicals in general terms.

1. Spin Multiplicity

The physical and chemical nature of molecular systems

having one or more unpaired electrons has been the subject of intense scientific investigation for some time. For example, Tschitschibabin's hydrocarbon, I, has been a source of controversy for the last half century and only recently has it been resolved.[1]



I

One of the more interesting properties of molecular systems containing unpaired electrons is the spin multiplicity resulting from the coupling possibilities of the respective electron spin vectors. It is a well established fact that a single electron can have two spin states.[2] If any arbitrary direction (e.g. z axis) is chosen, the component of the electron spin angular momentum in this direction will be restricted to two values which are given by $m_s\,(h/2\pi)$, where m_s is the spin quantum number and can have only two values, $\pm\frac{1}{2}$. The normalized wave function of the spin state with $m_s=+\frac{1}{2}$ is α while the normalized wave function for $m_s=-\frac{1}{2}$ is denoted by β. The operators for electron spin angular momentum and its component in the z direction are $\bar{S}$ and $\bar{S}_z$, respectively, and are shown in Equations 1 and 2.

$$\bar{S}^2\alpha = \tfrac{1}{2}(\tfrac{1}{2}+1)(h/2\pi)^2\alpha \; ; \quad \bar{S}_z\alpha = +\tfrac{1}{2}(h/2\pi)\alpha \qquad (1)$$

$$\bar{S}^2\beta = \tfrac{1}{2}(\tfrac{1}{2}+1)(h/2\pi)^2\beta \; ; \quad \bar{S}_z\beta = -\tfrac{1}{2}(h/2\pi)\beta \qquad (2)$$

Note that α and β are both eigenfunctions of $\bar{S}^2$ associated with the same eigenvalue and that they are eigenfunctions of $\bar{S}_z$ associated with different eigenvalues. The net result is that they are mutually orthogonal as shown mathematically in Equation 3. The term σ in Equation 3 represents the electron spin coordinate. Two electrons having the same spin function, either α or β, have parallel spins while two electrons with differing spin functions, α and β, have antiparallel spins by definition.

$$\int \alpha^*\beta \, d\sigma = \langle \alpha \mid \beta \rangle \qquad (3)$$

Extending this treatment to atoms or molecules having two or more electrons the $\bar{S}^2$ and $\bar{S}_z$ operators are defined as the sum of the one electron operators as shown in Equations 4 and 5.

$$S^2 = S_1^2 + S_2^2 + \cdots \qquad (4)$$

$$S_z = S_{z1} + S_{z2} + S_{z3} + \cdots \qquad (5)$$

These operators will have eigenfunctions F which must satisfy the conditions defined in Equations 6 and 7 where s is the total electron spin for the system. The term s can have integral, zero and half integral values and for each value of s the corresponding values of m_s are given by Equation 8. Obviously, for any given s there will be 2s+1 values of m_s; hence, the electron spin multiplicity of the system is simply 2s+1. For example, states having

s=0, $\frac{1}{2}$ and 1 will have corresponding multiplicities of 1,2 and 3, respectively. These are known as the singlet, doublet and triplet states.

$$\bar{S}^2 F = s(s+1)(h/2\pi)^2 F \tag{6}$$

$$\bar{S}_z F = m_s (h/2\pi) F \tag{7}$$

$$M_s = s,\ s-1 \ \ldots\ (s-1),\ -s \tag{8}$$

For the one electron situation,[3] $s=\frac{1}{2}$ and the system has a doublet spin state with the wavefunctions α and β. In the two electron case (arbitrarily labeled 1 and 2) there are four possible spin functions $\alpha(1)\alpha(2)$, $\alpha(1)\beta(2)$, $\beta(1)\alpha(2)$ and $\beta(1)\beta(2)$. It can be shown that $\alpha(1)\beta(2)$ and $\beta(1)\alpha(2)$ do not satisfy equation 6 and hence are not true spin state functions; however, symmetry combinations of these two functions are true wavefunctions. The normalized spin state functions which are all eigenfunctions of $\bar{S}^2$ and $\bar{S}_z$ are listed below:

	s	m_s	
$F_{1,1} = \alpha(1)\alpha(2)$	1	1	
$F_{1,0} = \sqrt{\frac{1}{2}}\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}$	1	0	Triplets (T)
$F_{1,-1} = \beta(1)\beta(2)$	1	-1	
$F_{0,0} = \sqrt{\frac{1}{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$	0	0	Singlet (S)

Again these spin state functions are mutually orthogonal. If the labels of the electrons are interchanged, it is found that the singlet wavefunction is multiplied by -1 and is antisymmetric with respect to electron exchange. If an identical operation is carried

out on the triplet, no change occurs and the function is symmetric with respect to electron exchange.

The orbital motion of the electrons in the central field of an atom results in an orbital angular momentum which is quantized and is found to have a magnitude of $M = l(l+1)^{\frac{1}{2}} (h/2\pi)$ where l can have zero and integral values. Again choosing the z axis as an arbitrary direction, the component of the orbital angular momentum in this direction is quantized and has the values $M_z = m_l \cdot (h/2\pi)$ where $m_l = l, l-1, \ldots, 0, \ldots, -(l-1), -l$. The operators for the orbital angular momentum and its component in the z direction are $\bar{L}$ and $\bar{L}_z$, respectively. The conditions of Equations 9 and 10 must be met if an electronic space function ψ_e is to be an eigenfunction of $\bar{L}^2$ and $\bar{L}_z$.

$$\bar{L}^2 \psi_e = l(l+1) (h/2\pi)^2 \psi_e \tag{9}$$

$$\bar{L}_z \psi_e = m_l (h/2\pi) \psi_e \tag{10}$$

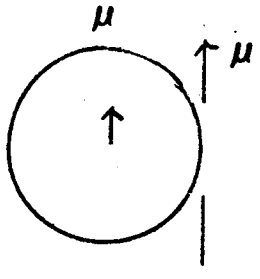
Due to the charge of the electron a magnetic moment, μ, accompanies the orbital angular momentum. Again choosing the z direction arbitrarily, the magnitude of μ is given by Equation 11.

$$\mu = (e/2mc) M_z = (e/2mc) m_l (h/2\pi) \tag{11}$$

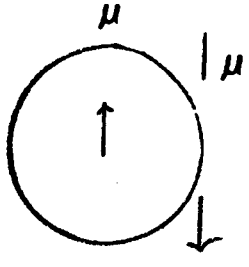
In a similar manner the spin angular momentum is accompanied by a magnetic moment, μ_s, which has its magnitude in the z direction given by Equation 12.

$$\mu_s = (e/mc) \cdot m_s (h/2\pi) \tag{12}$$

The interaction of μ_s with the magnetic field produced by the orbital motion of the electrons is known as spin-orbit coupling and was first proposed by Goudsmit and Uhlenbeck[3] in order to explain the fine structure in the atomic spectra of alkali metals.[2] Often the single line predicted by the Bohr model of the atom was actually found to consist of two closely spaced lines or a doublet. The explanation in simple terms is that s and m can be aligned either with each other or against each other as shown in Structures II and III, respectively. The electron will have two sublevels available at each energy level. In practice spin-orbit coupling is seldom of significance except when heavy atoms are involved, and as a result, s and m_s are good quantum numbers for molecules consisting of light atoms.



II



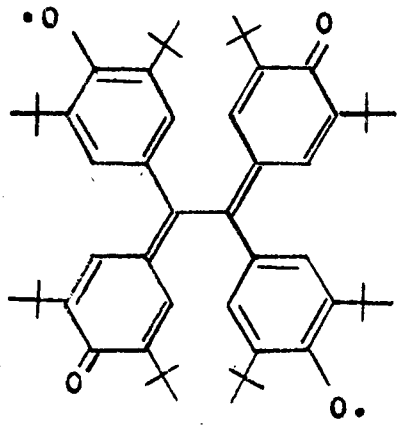
III

2. Definitions of Diradicals

The term diradical has in general been interpreted as describing systems which can be written with two unpaired electrons. On further scrutiny it can be seen that this description

is woefully inadequate since it encompasses a wide variety of chemical systems in which the amount of the "unpairing" of the electrons varies with the method of observation.[4] Salem and Rowland[4] have recently cataloged a number of commonly used but inadequate definitions of diradicals which will be described in the following paragraphs.

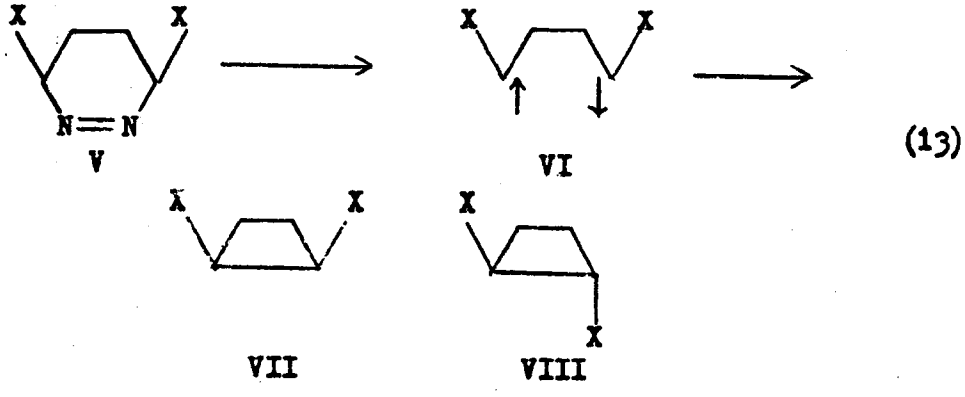
To the esr spectroscopist a diradical is a species exhibiting an esr spectrum characteristic of two doublets as opposed to one corresponding to a triplet. This will be the case whenever the interaction between the odd electrons is smaller than the hyperfine interaction between odd electron spin and nuclear spin. Using this line of reasoning a simple way to reduce electronic interaction is simply to move the electrons away from each other. Thus, bisgalvinoxyl, IV, shows a spectrum of two doublets. However, this view suffers from several weaknesses.



IV

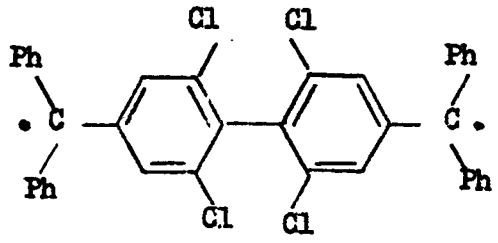
First, the electrons may still undergo weak residual coupling and be incorrectly assumed to have no interaction since the esr spectrum cannot detect it. (This interaction can be measured via hyperfine coupling however.) Also distance is not a valid criterion for weak electronic interaction since twisted (90°) singlet ethylene has a weak electron interaction.

A second point of view would require that unpaired electrons have parallel spins (e.g. all diradicals must be triplets) and is clearly inadequate since singlets commonly demonstrate biradical character. The final point of view is that held by the organic chemist who commonly recognizes diradical behavior by the loss of configuration occurring in a chemical reaction. Equation 13 illustrates a typical example in which structure VI would be an intermediate where rotation about the terminal bonds is faster than bond formation. However, it is possible for the diradical to be formed yet configuration maintained, if there is a large steric barrier to internal rotation. Further, this view essentially ignores multiplicity.



(13)

Clearly, then, the amount of electronic interaction between the unpaired electrons is of extreme importance. In the case of no electronic interaction the system is best described as a double radical. Such a system should exhibit spin paramagnetism and undergo complete separation of the charge centers of the two electrons. It should be noted that systems which fulfill these conditions are rare. Compounds IV (p 7) and IX are examples of true double radicals.[1]



IX

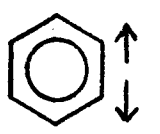
All double radicals and triplets exhibit spin paramagnetism whereas singlets do not.[5] Further the magnitude of the separation of the charge of the two electrons serves as a useful measure of the biradical nature displayed by a particular species, i.e., the larger the separation of charge in a singlet or triplet, the more biradical character the system has. A triplet normally has a greater separation of charge than a singlet derived from the same electron configuration, although on occasion the difference may be quite small.[5]

Salem and Rowland have chosen to define a diradical in more general and practical terms in order to clarify what is meant by diradical. Their definition is: "Diradicals are molecules with two (weakly interacting) odd electrons in degenerate or nearly degenerate molecular orbitals."

3. Homosymmetric and Heterosymmetric Diradicals

Of special interest to the discussion here are the homosymmetric and heterosymmetric diradicals as described by Salem and Rowland.[4] A homosymmetric diradical has been defined as any species in which the degenerate or nearly degenerate orbitals ϕ_A and ϕ_B are related by some symmetry element.

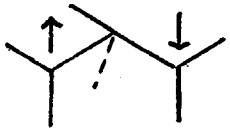
Examples of "homosymmetric" diradicals are o-dehydrobenzene, X, the trimethylenes, XIa and XIb, the tetramethylenes, XIIa and XIIb, and the triplet and singlet forms of twisted ethylene, XIIIa and XIIIb.



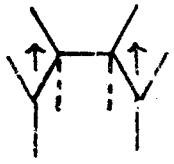
X



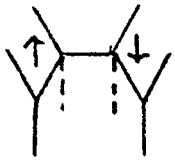
XIa



XIb



XIIa



XIIb

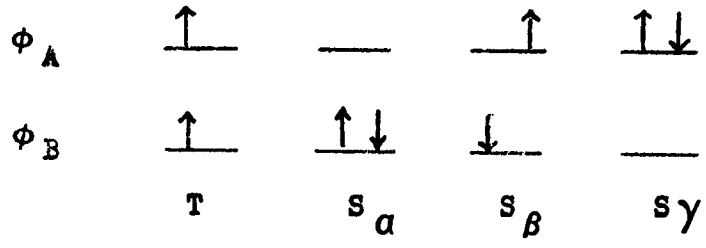


XIIIa



XIIIb

In the general case where $E_A \neq E_B$ there are two electrons and two discrete orbitals ϕ_A and ϕ_B and there are four ways in which the electrons can occupy the orbitals. This will again result in three singlets and one triplet.



If $E_A = E_B$ and electron repulsion terms are neglected, the result is four energetically equivalent states, again one triplet and three singlets. When electron repulsion terms are included these four states become nonequivalent with the triplet being the lowest in energy (ground state). The relative energies of these states are diagrammed below.

$\frac{1}{\sqrt{2}}(\phi_A^2 + \phi_B^2)$ ionic Singlet S_γ

$\phi_A \phi_A$ ionic Singlet S_β

$\frac{1}{\sqrt{2}}(\phi_A^2 - \phi_B^2)$ covalent Singlet S_α

$^3\phi_A \phi_B$ covalent Triplet T

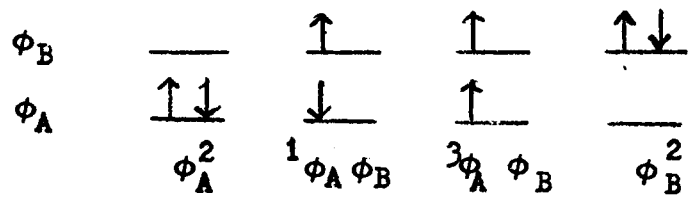
The relative ordering of the energy levels described above can be altered significantly if Jahn-Teller distortion occurs. The Jahn-Teller theorem dictates that orbital degeneracy in a symmetrical nonlinear molecule will be removed by some small distortion (vibration). Further, this distortion will produce a more stable conformation.[5] If these distortion are large enough then the singlet, S_a, can become the ground state.[6] The case of cyclobutadiene or [4]-annulene, XIV, while not homosymmetric, offers an interesting example of the effect of Jahn-Teller distortions on ground state multiplicity.[7] All calculations predict cyclobutadiene to have a ground state triplet if the molecule has a square geometry; however, the ground state is found to be a singlet of square geometry. A plausible explanation is that Jahn-Teller distortions have caused the molecule to have a less symmetrical geometry in which the singlet is the ground state.[5]

Now consider the heterosymmetric diradical which is defined[4] as "any species in which the odd orbitals Φ_A and Φ_B are not related by some element of symmetry." Examples of "heterosymmetric" diradicals are the lowest $n \rightarrow \pi^*$ triplet states of dienes, XV, the ground states of methylene, XVI, trimethylene, XIc, cyclobutadiene, XIV, and 1,8-naphthoquinodimethane, XVII.



XIV XV XVI XIc XVII

Thus, members of this molecular category have two odd electrons and two orbitals ϕ_A and ϕ_B. The electrons are able to occupy these orbitals in four possible ways: ϕ_A^2, $\phi_A \phi_B$ (singlet or triplet), and ϕ_B^2 or three singlets and one triplet.



In general, the resultant energies of these states can be ordered as shown in Figure 1a. The term μ in Figure 1 is a mixing parameter to define the particular combination of ϕ_A and ϕ_B. The special case where $E_A = E_B$ is described in Figure 1b. In either case the ground state is a triplet. Note that in Figure 1 the ionic states are actually zwitterions since the covalent terms are either absent or outweighed by the ionic terms.

B. Ground State Triplets

1. Introduction

A ground state triplet can occur whenever the following criteria are met in a molecule:[5]

a) there are an even number of electrons.

b) the highest occupied molecular orbital (HOMO) is at least doubly degenerate.

c) the degenerate HOMO's are partially filled.

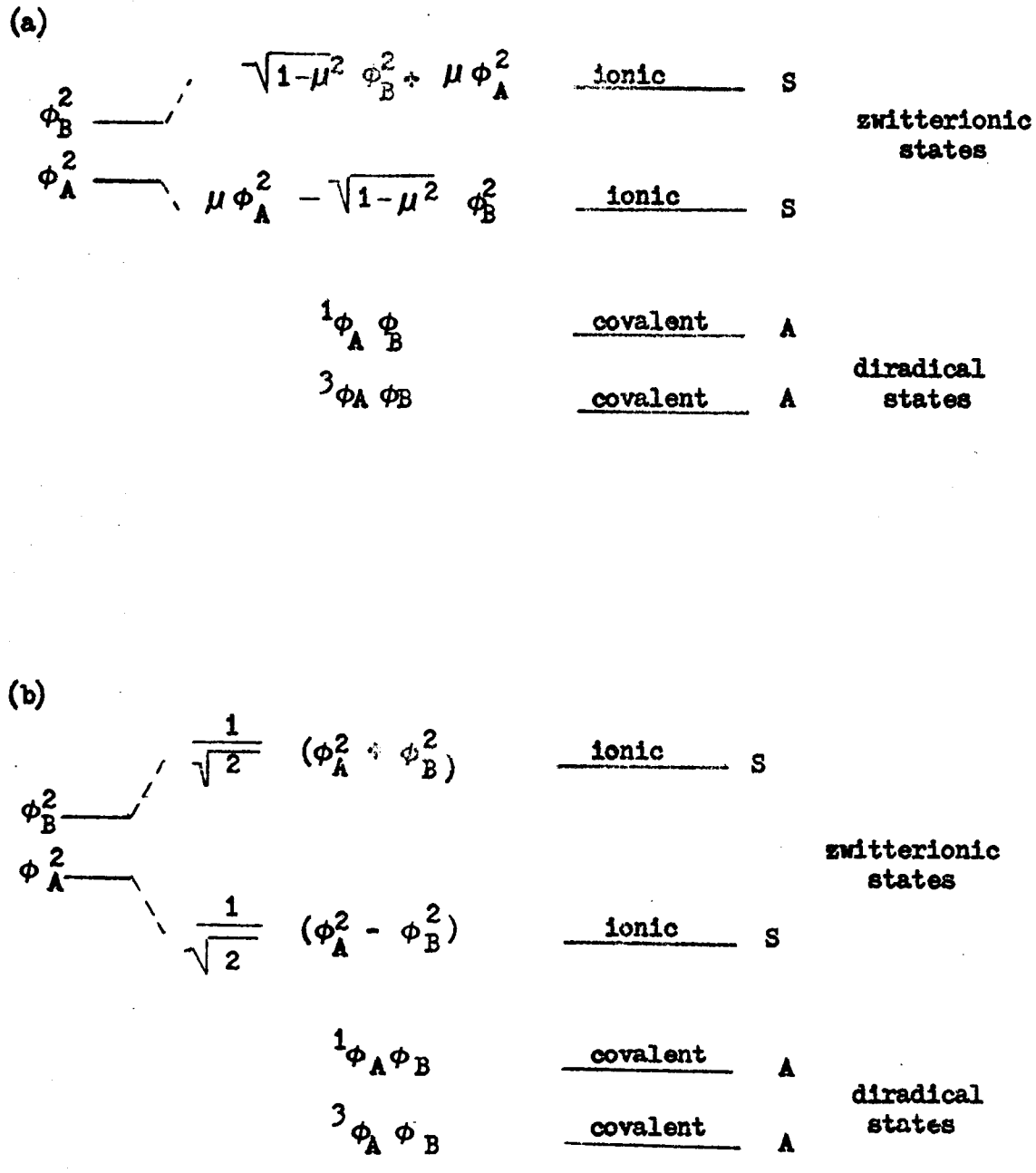
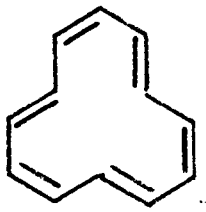


Figure 1. Energy levels of heterosymmetric diradicals.
(a) $E_A \neq E_B$ $(1 \geq \mu \geq 1/2)$; (b) $E_A = E_B$ (accidental degeneracy) $(\mu = 1/\sqrt{2})$.

In reality the second requirement is found to be too rigid. Approximate degeneracy is sufficient provided that the exchange energy associated with the triplet state is greater than the difference between the degenerate MO's.

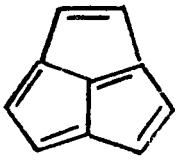
It should be that any alternant hydrocarbon having $4n$ electrons and which has a threefold or higher axis of symmetry would be expected to have a triplet ground state.[5] Some examples of molecules which meet these criteria are cyclobutadiene,[7] XVII (p 12), [12]-annulene, XVIII,[8] cyclooctatetraene, XIX,[8] tetramethyleneethane, XX,[9] acepentalene, XXI,[5] and the cyclopentadienyl cation, XXII.



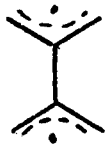
XVIII



XIX



XXI

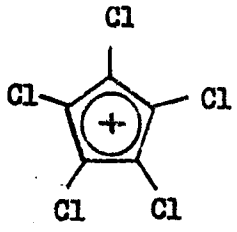


XX

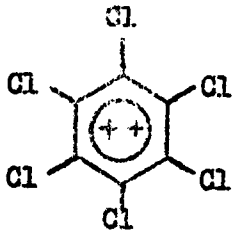


XXII

That the preceding generalization is true is supported by the esr spectra of XXIII and XXIV both of which are ground state triplets.[10,4] Further, since cyclooctatetraene is not planar, a ground state triplet is not observed in this case.

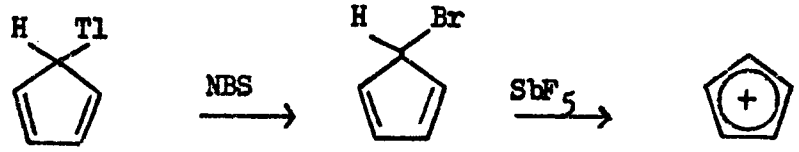


XXIII



XXIV

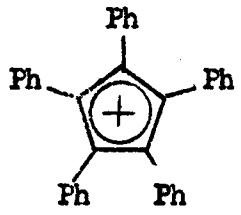
The unsubstituted cyclopentadienyl cation,[12] XXII, (p 15), has recently been prepared as shown in Equation 14. The esr spectrum and accompanying Curie law studies indicate that the unsubstituted cyclopentadienyl cation is indeed a ground state triplet as indicated by the above generalization. The value of D for this system is somewhat less than the $0.1495cm^{-1}$ value observed for $C_5Cl_5^{+1}$ since XXII is less delocalized than $C_5Cl_5^{+}$. The D value is a measure of the interaction between the two unpaired electrons and this term becomes smaller as the electrons become more distant from one another.



XXV XXVI XXII (14)

However, when the substituents are phenyl groups instead of chlorine as in XXVII, the molecule is a ground state singlet[6] with a low lying triplet approximately 1 kcal/mole higher in energy.

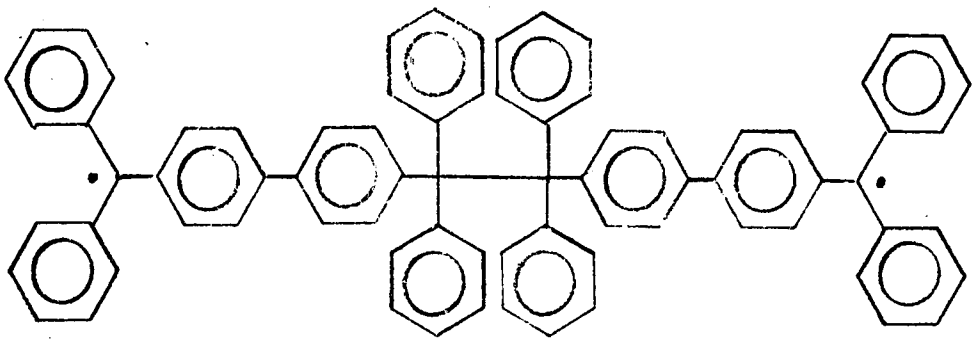
Apparently the crowding of the phenyl groups destroys the symmetry of the molecule and the degeneracy of the HOMO's while the size has reduced the Fermi correlation energy of the triplet[4].



XXVII

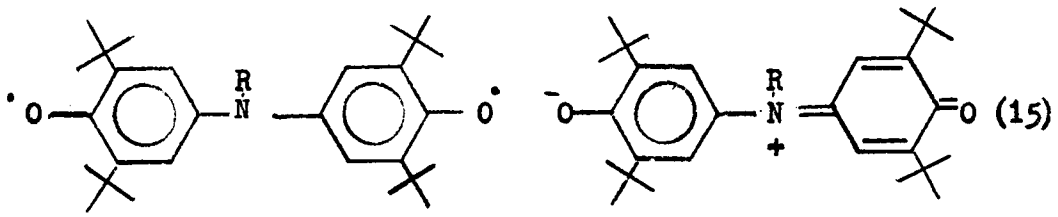
Additional examples of diradicals which have well-known triplet states are the lowest $n \longrightarrow \pi^*$ states of dienes and benzene and ground states of molecular oxygen[4], nitrene[4], trimethylene[1], twisted ethylene[4] and trimethylenemethane.[14]

The long standing controversy over the ground state of Tschitschibabin's hydrocarbon, I (p 2), has recently been resolved[1]. For years this compound was believed to be a typical conjugated biradical. Solutions of the hydrocarbon gave high resolution epr spectra assumed to be derived from monomeric, I (p 2). Waring and Sloan[15] demonstrated that the compound exists as a dimer and/or polymer. Further the species responsible for the epr spectrum was shown to be a p-biphenylyldiphenylmethyl radical, XXVIII, formed from the dimerization and/or polymerization of I, (p 2). The actual ground state of monomeric I is a singlet although a thermally populated triplet can be observed in the solid state.[1]



XXVIII

An extremely interesting triplet-singlet interconversion is the equilibrium of XXIXa and XXIXb. In this instance changing the hybridization from sp^3 to sp^2 on the nitrogen atom is sufficient to convert the paramagnetic triplet ground state, XXIXa, into a diamagnetic closed shell system, XXIXb.[4]

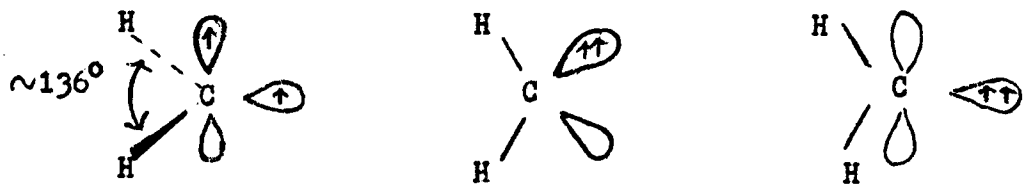


XXIXa XXIXb (15)

2. Methylene

Methylene is perhaps the best known organic diradical species. Herzberg reported the spectroscopic observation of three triplet methylenes in 1961. Each of these triplets had a different geometry and energy, but it was not possible at that time to

determine conclusively which of the three triplets was the ground state.[16] In 1970, Wasserman and co-workers reported that the ground state of methylene was the highly bent triplet species having an H-C-H bond angle of $136 \pm 8^{\circ}$, XXX.[17] There is also a low-lying excited singlet which has a bent H-C-H angle ($\sim 103^{\circ}$). The singlet can be pictured as either an sp^3 hybridized carbon atom with two electrons in one sp^3 orbital and a vacant orbital, XXXI, or an sp^2 hybridized carbon with the electron pair in an sp^2 orbital and a vacant p orbital, XXXII. The bond angle favors XXXI but the analogy with carbonium ions favors XXXII.

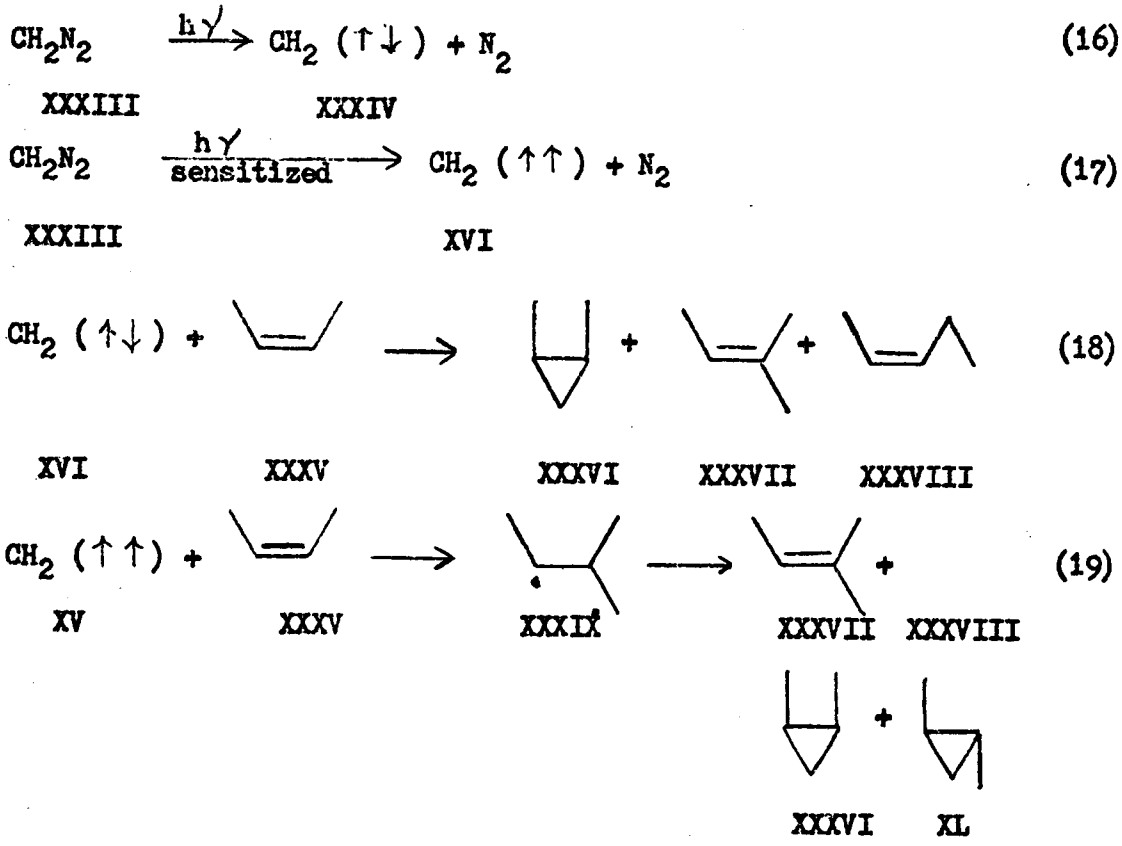


XXX XXXI XXXII

Experimentally direct photolysis of either ketene or diazomethane gives singlet methylene which is found to add stereospecifically to olefins and to undergo random insertion into C-H bonds. In contrast photochemical decomposition of ketene or diazomethane sensitized by mercury in the gas phase[18] and acetophenone in solution[19] gives triplet methylene which is found to add nonstereospecifically to olefins and which gives few C-H insertion products.

At this point it is appropriate to introduce Skell's hypothesis.[20] This is an intuitive argument which states that triplet species should add to olefins in a stepwise fashion due to

the necessity of spin inversion in the triplet diradical intermediate, XXXIX, before bond formation can occur. Presumably bond rotation can occur faster than the spin flip necessary for bond formation in the biradical intermediate, hence the lack of stereospecificity. On the other hand the singlet should be able to form bonds directly in a concerted fashion and this would result in stereospecific addition to double bonds.



The commonly used probe for triplet or singlet methylene assumes that Skell's hypothesis is correct and observes the products obtained in the reaction of the methylene with each geometric isomer of an olefin. Triplet methylene products from cis-2-butene would

be cis- and trans-1,2-dimethylcyclopropane, cis-2-pentene and 3-methyl-2-butene. Likewise, the singlet would produce cis-1,2-dimethylcyclopropane, cis-2-pentene and 3-methyle-2-butene. These expectations are borne out experimentally with the added observation that the formation of triplet products is completely inhibited (or quenched) by the presence of oxygen accompanied by the enhancement of singlet product formation.

The gas phase photolysis of diazomethane has been the source of some confusion in recent years due to large pressure and wavelength effects on the reactions.[21,22,23] Excited singlet diazomethane is formed on photolysis of diazomethane. The excited species then decomposes giving singlet methylene. In the test of Skell's hypothesis, singlet methylene can either undergo intersystem crossing to give the ground state triplet or it can react with cis-2-butene to form a vibrationally excited or "hot" cyclopropane which can rearrange unless it is collisionally stabilized. Herzberg[16] has demonstrated intersystem crossing to be very inefficient, requiring a number of collisions with inert molecules before occurring.

Bader and Generosa[23] have considerably enhanced the overall understanding of the effect of inert gas pressure on the gas phase photolysis of diazomethane. They photolyzed mixtures of diazomethane and cis-2-butene in the presence of varying pressures of added gases. The product yields were determined as a function of gas pressure and it was found that argon, nitrogen, neon and carbon tetrafluoride all produce minima in plots of percent of any given

product versus gas pressure. Further, corresponding plots of singlet products gave maxima at the same pressures where the minima occurred. This observation leads to two simultaneous collisional deactivation mechanisms being postulated. The first must be an efficient removal of some species which gives nonstereospecific products and can be attributed to collisional stabilization of "hot" cyclopropane formed by singlet addition to cis-2-butene. The second process is a relatively inefficient production of an intermediate which gives nonstereospecific products and may be considered a result of intersystem crossing of singlet methylene to triplet methylene.

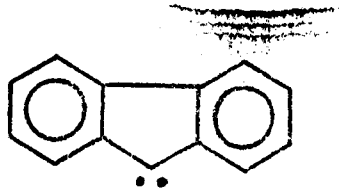
It is interesting to note that in the addition of triplet methylene to cis and trans olefins, the same ratio of cis and trans cyclopropanes is not observed although they should have a common intermediate. This apparent anomaly can be explained if one assumes that the rate of spin inversion necessary for ring formation occurs at a rate comparable to carbon-carbon bond rotation.[24]

It has been observed in the gas-phase photolysis of ketene that triplet methylene can be a primary product depending on the wavelength used.[25,26] Presumably this is because the decomposition of low vibrational levels of singlet ketene is slow enough to permit intersystem crossing to take place giving triplet ketene and subsequently triplet methylene. The yield of triplet methylene varies from 0% at 3000Å to 100% at 4358Å. Interestingly, no triplet methylene is formed even at long wavelengths in solution indicating

that some deactivation process operates on a triplet methylene precursor.

As a further complication Cundall and Davies[27] have reported that ketene itself sensitizes the cis-trans isomerization of olefins This effect is important particularly at high olefin pressures; hence, "triplet" products could conceivably be observed from purely singlet methylene if the concentration of olefin were high.

If the hydrogens in methylene are replaced by halogens as in $:CF_2$ and $:CCl_2$, the bent singlet is stabilized to the point where it becomes the ground state.[28,29,30] Compound XLI offers an interesting example of a carbene having a bent ground state triplet in which the angle about the divalent carbon is 140-150°.[26]

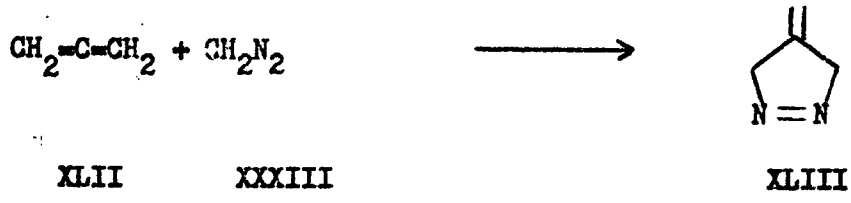


XLI

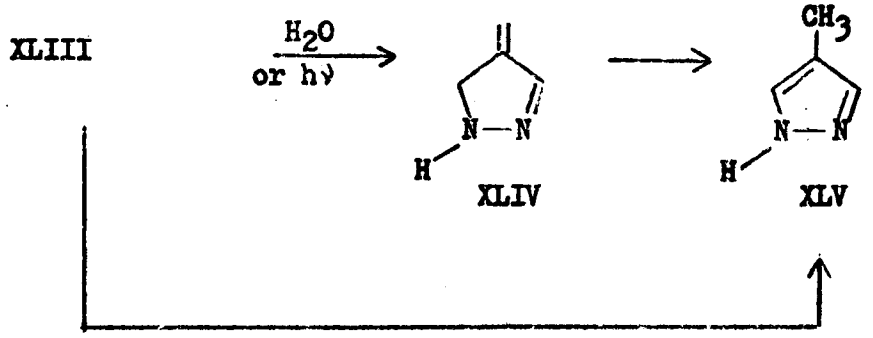
3. Trimethylenemethane

Trimethylenemethane is a system of unusual theoretical interest.[14] It is a ground state triplet in which the central carbon atom attains the highest possible mobile bond order for a sp^2 carbon atom and it is the basis for all Hückel molecular orbital calculations of bond order and spin density.[14] Chemically it has been assumed to be an intermediate in the formation and rearrangement of methylenecyclopropanes.

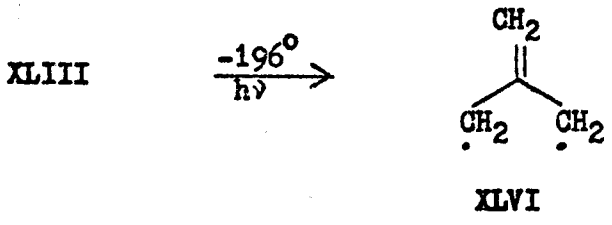
4-Methylene-Δ^1-pyrazoline, XLIII, is an ideal precursor for the generation of trimethylenemethane, XLVI, and can be synthesized by the reaction of diazomethane and allene.[31] Anhydrous, oxygen-free conditions are necessary to avoid rearrangement of XLIII into XLVI and oxidation to undesirable side-products.



XLII XXXIII XLIII (20)



XLIII XLIV XLV (21)



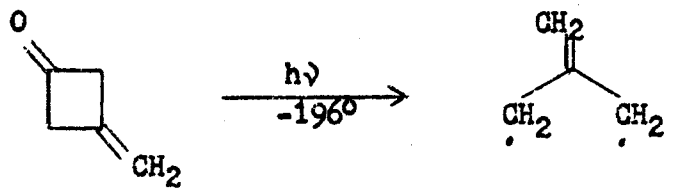
XLIII XLVI (22)

At ambient temperatures photolysis of XLIII gives XLV; however, low-temperature photolysis of a glassy solution of XLIII resulted in a species exhibiting an esr spectrum attributable to triplet trimethylenemethane.[32] The four lines of the spectrum due to

trimethylenemethane were found to be stable over a period of months as long as liquid nitrogen temperatures were maintained. Elevation of the temperature to -150° resulted in the rapid disappearance of the triplet spectrum. In addition to the lines due to the triplet species there is an intense line in the center of the spectrum which is probably due to stable monoradicals. The E value, a measure of the system's symmetry, was found to be zero indicating a highly symmetrical species. The splitting between the outermost two lines or D value is $0.025cm^{-1}$ which is much smaller than that observed in triplet naphthalene or diphenylmethane.

As stated above the observed triplet spectrum consisted of four lines. There are a possible six lines which could be observed since there could be two lines for each Cartesian coordinate. The observation of only four lines is consistent with a species having two of the axes equivalent by symmetry. Trimethylenemethane then must have at least C_3 and probably D_{3h} symmetry in the triplet.

Another synthetic approach to trimethylenemethane is via the low temperature photolysis of XLVII.[32] This procedure was found to produce a much stronger and cleaner spectrum than did photolysis of XLIII, (p 24). The central impurity line found when XLIII, (p 24), was photolyzed was absent and the spectrum was strong enough to allow the observation of the $\Delta m=2$ line at 1590G.



(23)

XLVII XLVI

In esr spectroscopy, absorption is found to occur when the microwave frequency is in exact resonance with the spin transition energies of the unpaired electrons. For free radical systems, only $m=\pm1$ transitions are allowed while for triplets the $m=\pm2$ transitions can also be observed at one half of the normal field strength. Figure 2 illustrates the dependence of the transition energies on the field strength for a molecular system having small zero-field splittings. The D and E values or zero field parameters arise from the spin Hamiltonian derived for the radical system involved. These zero-field parameters provide a measure of the zero field splittings shown in Figure 2 and provide a great deal of insight into the electronic configurations of triplet systems. As stated earlier, the D value is a measure of the interaction between the two spin-parallel electrons and diminishes as the electrons become more distant from each other. The E value is a function of the symmetry of the molecule.[24] More will be said about these zero-field parameters in later sections.

Single crystals of XLVII (p 25) could be grown thereby allowing the observation of the proton hyperfine spectrum on photolysis. The seven lines observed in this experiment and their intensity ratios indicate the interaction of six equivalent protons. The observed splitting between peaks is 8.9G in agreement with valence-bond predictions; however, Hückel theory does not take the negative spin density on the central carbon atom into account and predicts a value of 7.1G for this splitting. Thus far there

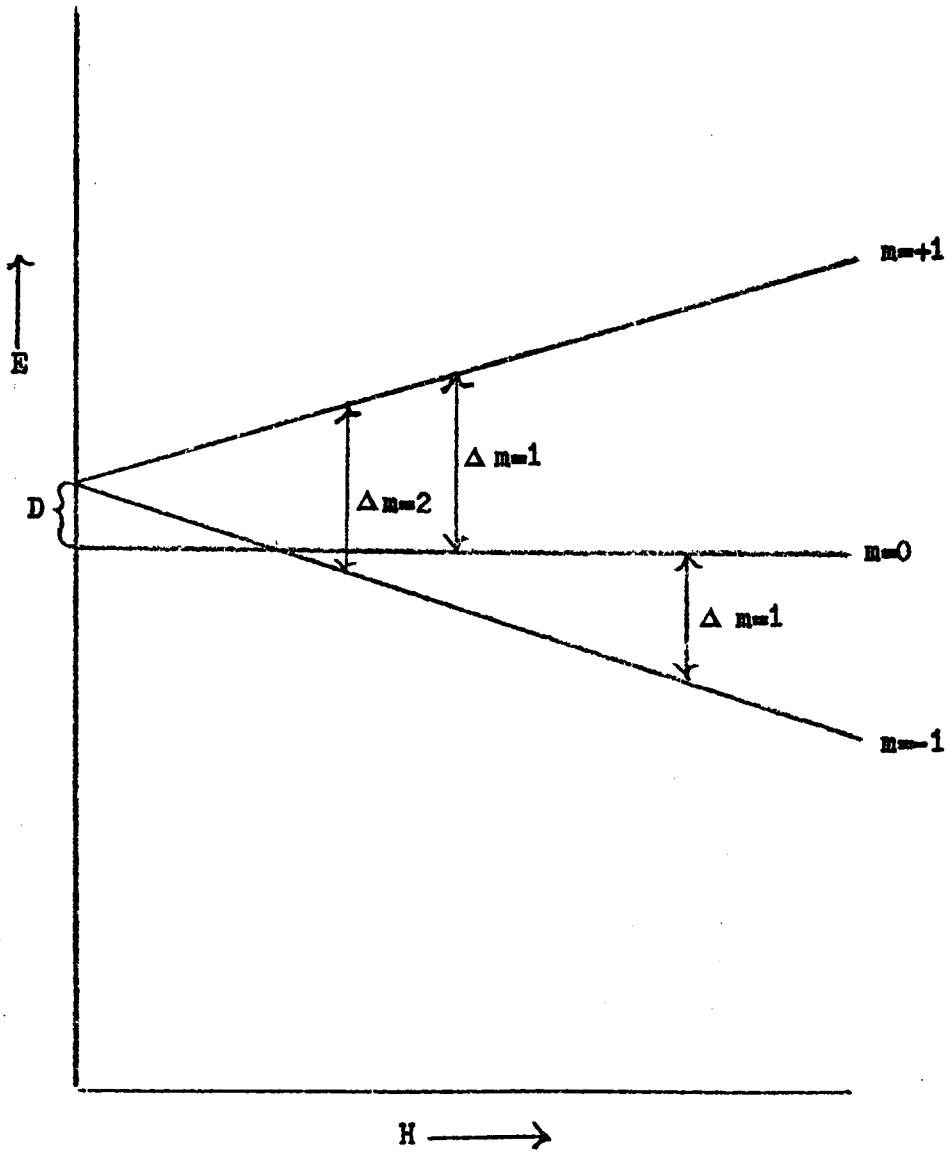
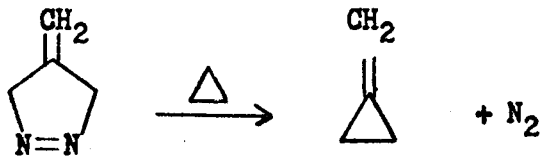


Figure 2. Dependence of transition energies on field strength for a system with small zero-field splittings between the unpaired electrons.

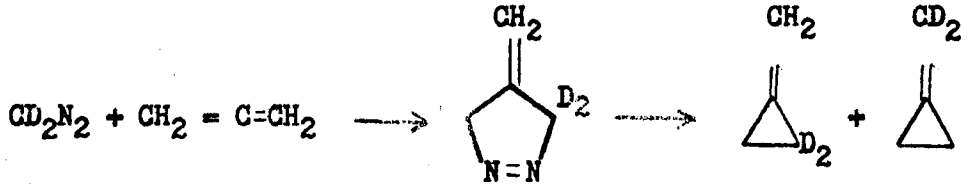
has been no evidence requiring trimethylenemethane to be planar (D_{3h}) although the data are consistent with such a geometry.

Crawford and Cameron studied the pyrolysis of XLIII and found the sole product to be methylene cyclopropane, XLVIII.[33] Kinetic studies of this reaction were undertaken and the activation parameters were subsequently determined. They found E_a = 32.6 kcal/mole and $S^{\neq}$ (250°) = -1.1 eu for the decomposition.



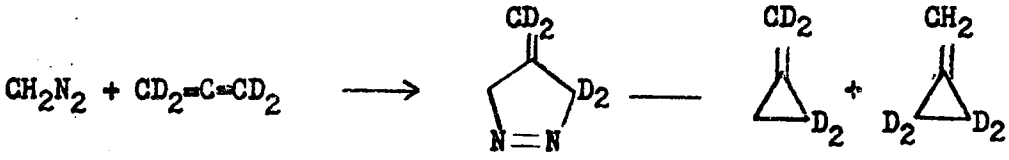
XLIII XLVIII (24)

In order to gain some insight into the symmetry of the intermediate, deuterium labelling was used and Compounds XLIII-d_2 and XLIII-d_4 were prepared.[33] These deuteriated compounds were pyrolyzed and the results are shown in Equations 25 and 26. The product ratios XLVIIIa/XLVIIIb and XLVIIIc/XLIIId while nonstatistical were consistent with a concerted loss of nitrogen to give trimethylenemethane which can then undergo bond rotation and subsequent ring closure. It was postulated that carbon-carbon bond rotation for CD_2 (k_D) is slower than for CH_2 (k_H), hence the nonstatistical deuterium distribution from a trimethylenemethane. The alternate mechanism involving step-wise loss of nitrogen was not consistent with the secondary deuterium isotope effect required by the decomposition of XLIII-d_2.



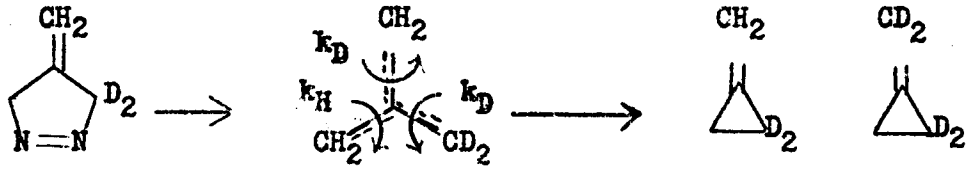
(25)

XXXIII-d_2 XLII XLIII-d_2 XLVIIIa XLVIIIb



(26)

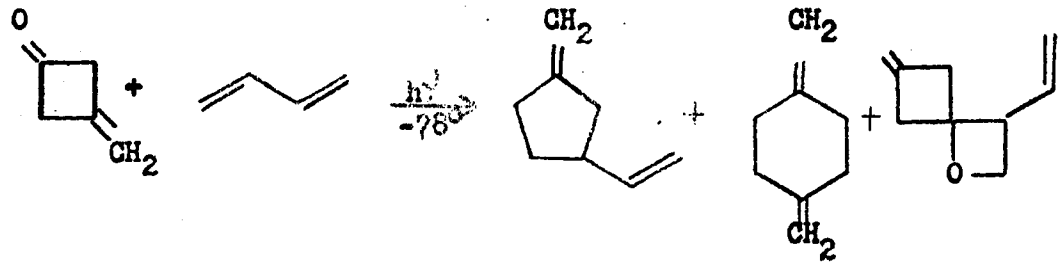
XXXIII XLII-d_4 XLIII-d_4 XLVIIIc XVLIIId



(27)

XLIII-d_2 XLIX XLVIIIa + XLVIIIb

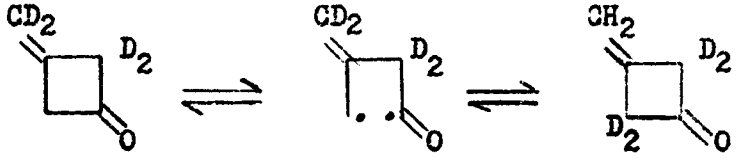
In addition to the direct observation of trimethylenemethane in epr studies, indirect observation by chemical trapping was undertaken. Negative results were obtained when XLVII was photolyzed in the presence of 1,1-diphenylethylene, 1,1-dimethoxyethylene, cyclopentene, furan and cyclopentadiene.[34] These attempts resulted in the formation of oxetanes instead of products derived from trimethylenemethane. Photolysis of XLVII in butadiene at -78° gave an adduct with butadiene and a product of self-trapping as shown in Equation 28.



(28)

XLVII L LI LII LIII

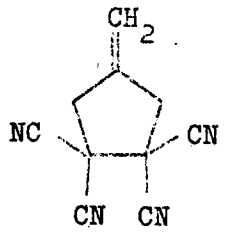
The deuterated ketone XLVII-d_4 was prepared to test the intermediacy of trimethylenemethane in the above reaction.[34] Photolysis of XLVII-d_4 in butadiene at -78° gave Compound LI with the four deuterium atoms of trimethylenemethane. Control experiments showed that recovered LVII-d_4 also had the deuterium atoms completely scrambled. This result can be pictured as arising from ring cleavage, bond rotation and reformation of the ring.



(29)

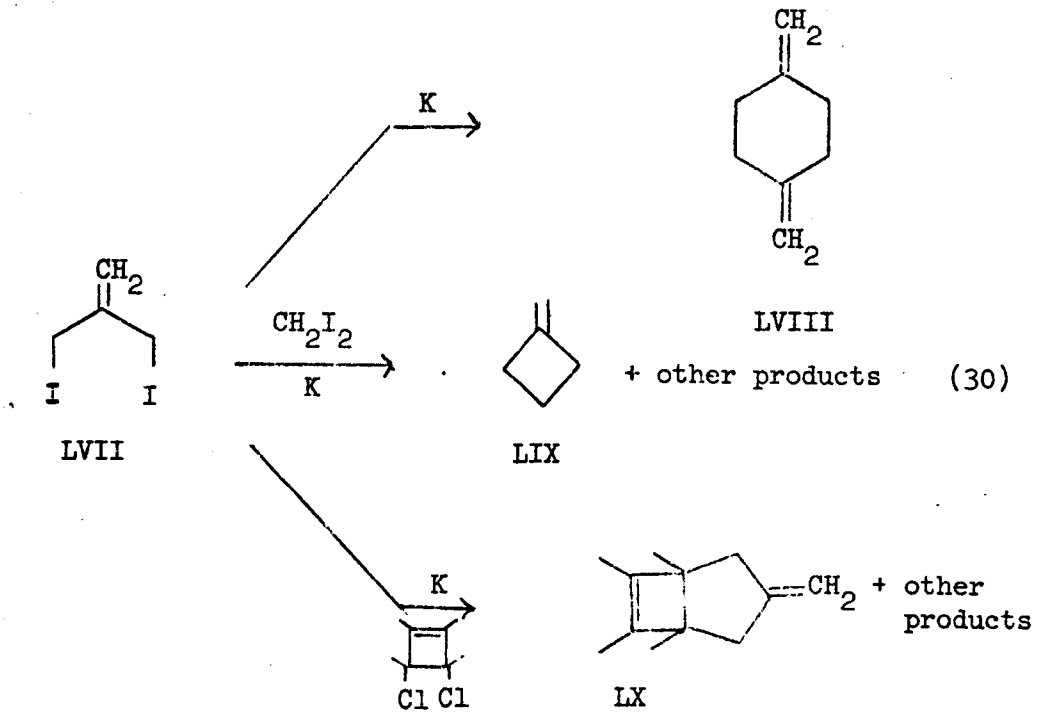
XLVII-d_4 LIX LV

As is the case with cyclobutadiene and many other unstable species, it is possible to prepare stable iron tricarbonyl complexes of trimethylenemethane.[35] Ward and Pettit[36] treated trimethylenemethane iron tricarbonyl with Ce^{4+} in the presence of tetracyanoethylene and obtained the 1:1 adduct LVI. Further they were able to isolate the iron and chromium complexes of trimethylenemethane.



LVI

Doerr and Skell[37,38] have studied the formation of trimethylenemethane from the reaction of LVII and alkali metals as shown in Equation 30. In the runs with trapping agents no dimers were obtained, and the isolation of Compounds LIX and LX indicates the trapping of trimethylenemethane, although the system is perhaps too complex to justify any attempt at dissection.

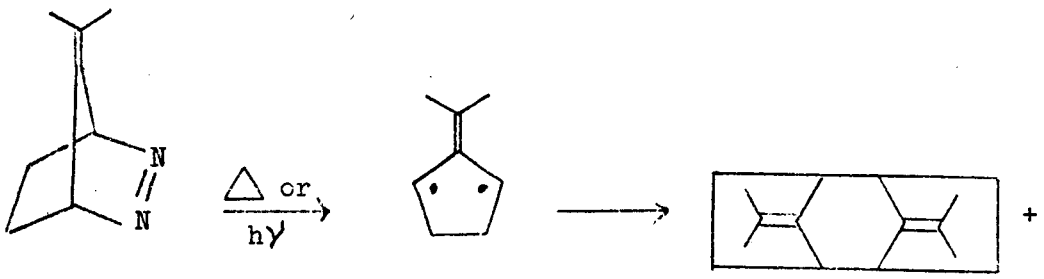


LVII LIX LVIII LX + other products (30)

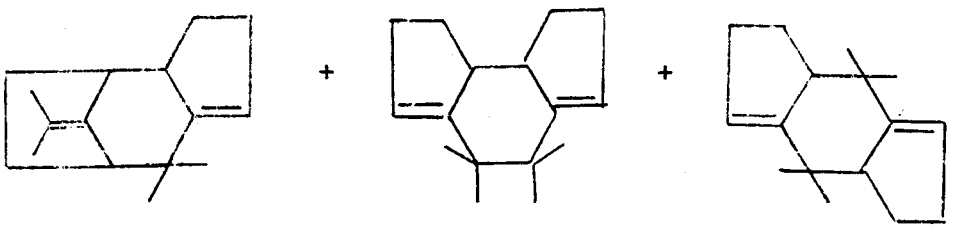
4. Bridged Trimethylenemethane

In a recent series of papers[39-43] Berson and co-workers

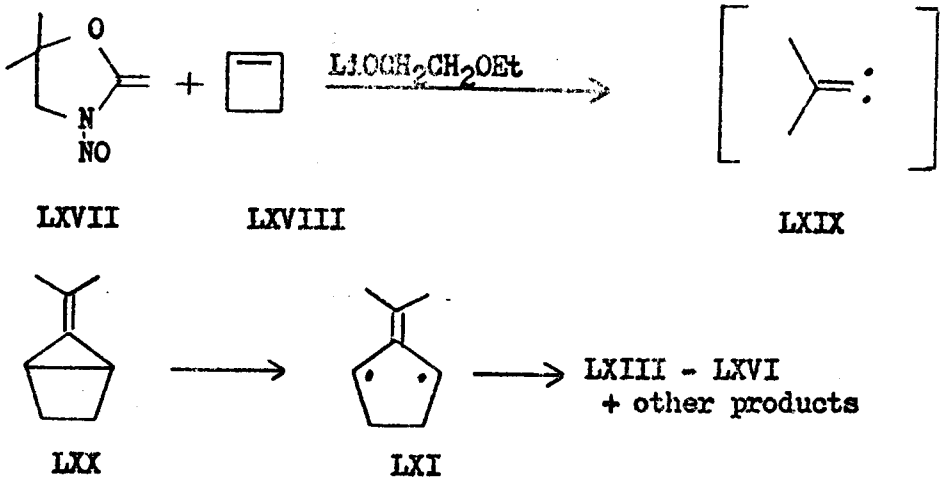
have studied Structure LXI, an unsymmetrically substituted trimethylenemethane. This system offers the possibility of studying the effect of symmetry on the ordering of the singlet and triplet energy levels. The necessary azo precursor LXII was prepared by conventional means and its decomposition studied thermally and photochemically.[39] Pyrolysis of LXII at 80° in the gas phase gave four dimeric products which were identified as Compounds LXIII-LXVI (stereochemistry unknown). Also photolysis of Compound LXII was found to give the same four dimeric products in the same relative percentages as thos obtained in the thermal reaction as well as other products. It was found that these same four dimeric products in the same relative percentages were formed in the reaction of dimethylvinylidene and cyclobutene. The simplest way to explain the formation of Compound LXIII-LXVI in this reaction is to postulate the intermediacy of LXI which arises as shown in Equation 32.



LXII LXI LXIII (31)



LXIV LXV LXVI



(32)

The above experimental results certainly point to a common intermediate such as LXI but do not prove its existence and direct observation of the intermediate would be much more convincing. In an attempt to observe LXI directly, a degassed solution of LXII in perfluoro(methylcyclohexane) was irradiated at 77°K and a triplet esr spectrum was obtained. This spectrum is attributed to LXI and consists of a strong six-line absorption centered near 3250G and a weak absorption near 1625G due to the half-field transition. The zero-field parameters for XLI are D=0.027cm^{-1} and E=0.0023 cm^{-1} compared to D=0.024cm^{-1} and E=0 for trimethylenemethane itself. The difference in the E values can be explained by the distortion of the D_{3h} symmetry of trimethylenemethane to C_{2v} in LXI.

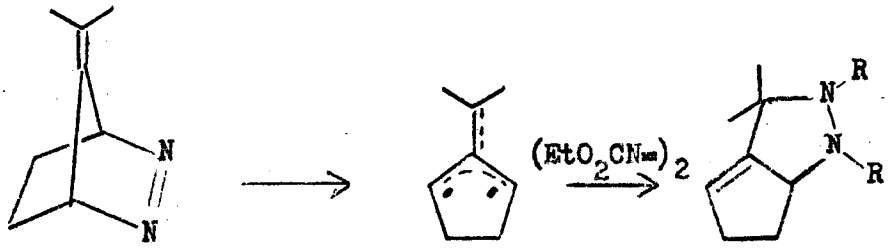
Conceptually the formation of the dimers could involve two singlets, two triplets or one singlet and one triplet. Note that although the presence of a triplet has been demonstrated by the esr data the actual involvement of a triplet species in the

reaction has not. The nmr spectra of solutions of LXII at temperatures ranging from 63.5° to 112° showed strong nuclear polarization emmission signals at positions corresponding to those of the nonpolarized absorption lines of the product dimers. Emission lines were in fact observed for nearly all of the product protons and not only at the positions corresponding to the sites of the carbon atoms of dimerization. Further no enhanced absorption lines were observed and the above behavior cannot be the result of a singlet-singlet dimerization. The chemically induced dynamic nuclear polarization (CIDNP) can be the result of either a triplet-triplet or a singlet-triplet dimerization. In any event the actual involvement of the triplet in product formation has been conclusively demonstrated.

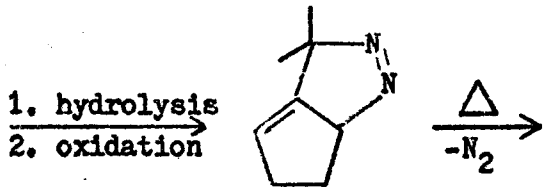
Closs has undertaken a theoretical study of CIDNP signals arising from triplet dimerization.[44] He concluded that triplet dimerization can give rise to CIDNP signals in which the polarizations orignate either in the region of weak interactions between the triplet molecules or in transitions of the resulting triplet biradicals if the exchange coupling is small enough.

In their study Berson, McDaniel, Corwin and Davis[40] found that it was possible to chemically trap intermediate LXI by the slow thermal decomposition of LXII in the presence of a large excess of the olefinic acceptor. Under these conditions the formation of the usual dimeric products could be almost completely suppressed depending on the efficiency of the trapping agent. Acetylenes were found to be poor trapping agents for this intermediate

as were simple olefins such as cyclohexene, dihydropyran and 1,2-diethoxyethylene. 1,3-Cyclohexadiene, 2,4-hexadiene, methyl acrylate, acrylonitrile and fumaronitrile were found to form adducts in high yield. An interesting example of this trapping reaction is the overall "azo transfer" accomplished using dimethyl azodicarboxylate followed by the usual hydrolysis, decarboxylation and oxidation procedure. Thermal decomposition of LXXII gives the same dimers in the same relative ratios as those obtained from the thermal decomposition of LXII.



LXII LXI LXXI



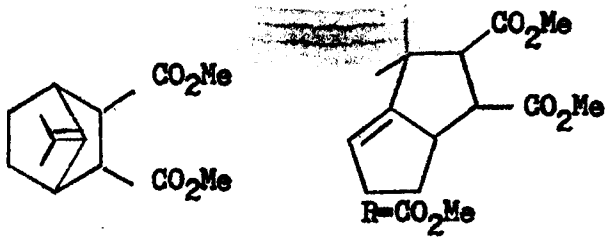
LXXII

(33)

dimers, XLII-XLV (p 32)

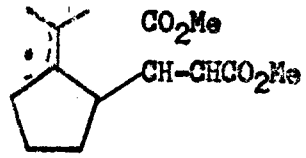
As a result of the two carbon bridge in LXI the adducts formed can be either bridged, LXXIII, or fused, LXXIV. Regiospecificity in the trapping reaction was found to be highly dependent upon the trapping agent used. For example either cis- or trans-

1,2-dichoroethylene gives a 10% yield of a cycloadduct mixture containing both fused and bridged products in a 1:1 ratio while fumaronitrile gives 83% isolated yield of fused adducts. Dimethyl maleate and dimethyl fumarate give a 95-100% yield of mixtures of fused and bridged cycloadducts. The product composition obtained from dimethyl maleate consists of the two fused adducts LXXIV with cis-carbomethoxy groups (27 and 36%), the corresponding fused adducts LXXIV with trans-carbomethoxy groups (11 and 8%) and the bridged adducts LXXIII endo-cis (1%) and trans (17%). Dimethyl fumarate in contrast gives essentially only trans adducts, fused, LXXIV, (57 and 33%) and bridged, LXXIII, (10%).



LXXIII LXXIV

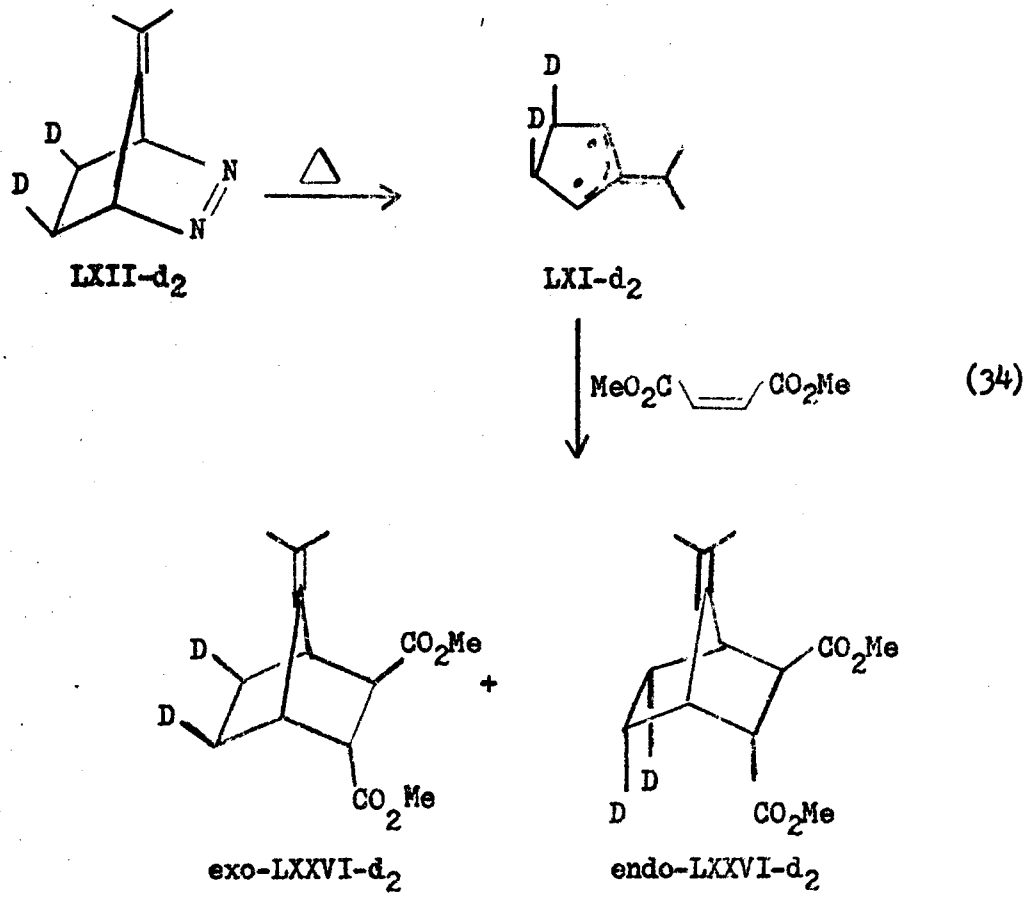
Clearly cis ⟶ trans crossover does occur in the maleate addition; however, a single long-lived diradical such as LXXV cannot be the intermediate in the maleate and fumarate addition since the same adduct mixture would have to result from each.



LXXV

In another part of this study Berson, McDaniel and Corwin[41] sought to elucidate the mechanism of the trapping reaction of LXI (p 33) with olefins. The rate determining step for the reaction was found to be the conversion of the azo compounds into an intermediate which can then form the four previously described dimers or react with a trapping agent to give the adducts discussed above. The azo decomposition under these conditions is zero order in the trapping agent; however, the product composition does depend on olefin concentration and more will be said about this aspect later.

In order to determine the stereochemistry of the intermediate, Compound LXII-d_2 was prepared. Thermal decomposition of LXII-d_2 in the presence of dimethyl maleate gave a variety of products from which Compounds exo- and endo- LXXVI-d_2 can be isolated. They were found to be formed in a 50:50 mixture indicating that any asymmetric species that may occur in the initial stages of the reaction becomes effectively symmetrical before trapping by the diylophile. If the trapping reaction is a two-step process then it cannot be detectably reversible since dimethyl maleate and dimethyl fumarate can be recovered from the reaction mixture without loss of stereochemistry.

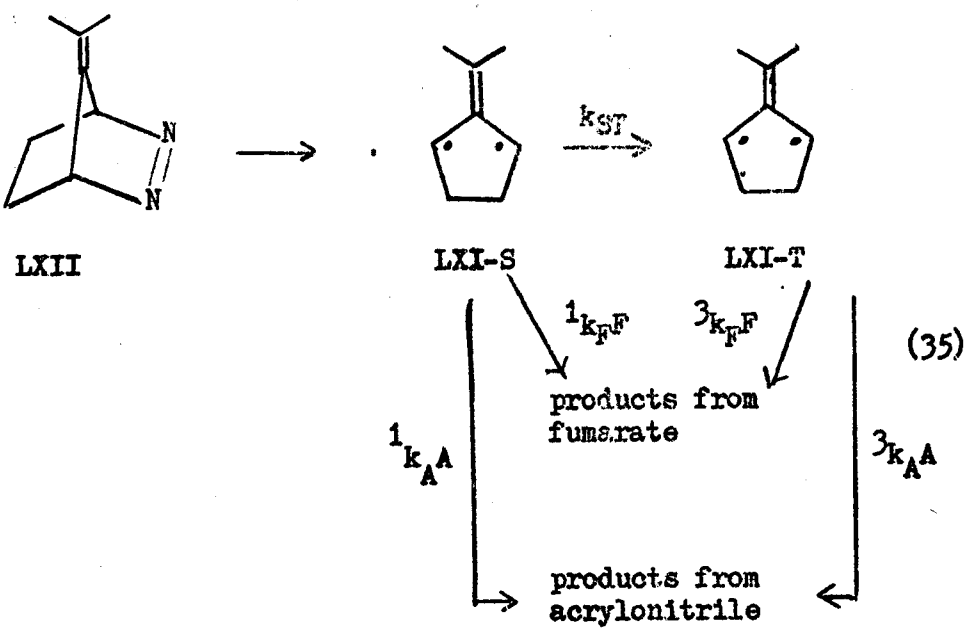


In order to determine the spin state of the reactive species in the cycloaddition, a CIDNP experiment was carried out using the azo compound in acetonitrile solution with fumaronitrile. Theory suggests that a triplet reacting with a singlet olefin could give an observable polarized product; however, no CIDNP signal was observed at all. This result does not exclude a triplet but it does suggest that the main reactive intermediate in this instance may be the singlet.

Dilution of the initial olefin concentration resulted in a marked increase in the amount of <u>cis</u> ⟶ <u>trans</u> crossover product obtained. This observation could be explained by the

involvement of two intermediates in the reaction; the first being a directly derived singlet which reacts stereospecifically and the other a slowly formed triplet reacting nonstereospecifically.

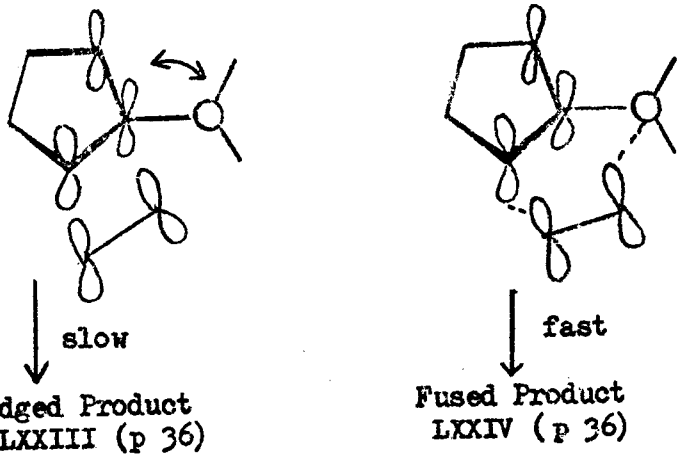
By careful study of the diylophilic reactivities of various compound toward LXI (p 32) followed by careful mathematical analysis, Berson, Duncan and Corwin[42,43] were able to learn a great deal more about the nature of the singlet and triplet in the trapping reactions described previously. In a series of competition experiments involving acrylonitrile versus dimethyl fumarate as trapping agents for LXI, it was found that the reactivity ratio (reactivity acrylonitrile/reactivity dimethyl fumarate) for the two diylophyls was constant at total olefin concentrations in excess of 1.5M. However, on dilution of the olefin concentration, the relative reactivities change dramatically and the reactivity ratio climbs steeply until at 0.01M total olefin concentration the ration has risen to seven times its high concentration limiting value. In addition it was found that a high concentration reactivity ratio can be restored in dilute solution by the addition of molecular oxygen. The following equation explains this behavior.



(35)

The singlet LXI-S is initially formed from the decomposition of LXII and can then either undergo trapping (^1k_AA and ^1k_FF) or intersystem crossing k_{ST} to the triplet which is then trapped (^3k_FF and ^3k_AA). At high olefin concentrations (1.5M) the intersystem crossing is too slow to compete with singlet trapping. Hence one observes a reactivity ratio which is characteristic of the singlet. However, at lower total olefin concentrations the intersystem crossing can occur and the triplet becomes increasingly more important. The effect of adding oxygen can be explained by molecular (triplet) oxygen interacting with the triplet in an efficient, selective spin-conserving and irreversible manner thereby removing the triplet before it can be trapped. It might be noted here that the observed singlet reactivities roughly parallel the Diels-Alder dienophilic reactivities for the olefins studied with cyclopentadiene.

Another interesting dilution phenomenon provided by the observation of Berson, Duncan and Corwin[42] is that the regiospecificity of the trapping reactions is also concentration dependent. In brief it was found that the cycloadditions involving triplet LXI-T (p 40) were sterically and orientationally nonspecific while the singlet LXI-S (p 40) reacted with high cis stereospecificity and high regiospecificity giving fused products. Berson et al.,[42] suggest that this result can be explained by the singlet having a bisected geometry which would produce a low bond order for the developing bond in the bridged product but not in the fused product while a planar geometry would have the opposite effect.

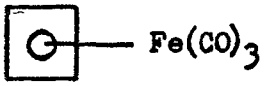


5. Cyclobutadiene

Cyclobutadiene or [4]-annulene, XIV (p 12), is predicted by Hückel theory to be a ground state triplet (p 15).[45] In contrast, the valence bond (VB) treatment predicts a ground state singlet with

appreciable resonance stabilization for cyclobutadiene. Further the VB method indicates that the ground state may prefer a rectangular D_{2h} symmetry over the higher D_{4h} square symmetry. On the other hand more sophisticated calculations indicate the triplet ground state to be favored over the square singlet. Unfortunately these calculations are not capable of predicting whether the square triplet or rectangular singlet is the more stable species although the energy difference should be small.[55] Modern concepts of aromaticity ascribe antiaromatic character to cyclobutadiene. That is, cyclobutadiene is expected to be resonance destabilized by cyclic conjugation. Dewar has calculated the increase in energy due to antiaromaticity to be 18 kcal/mole.[46]

Until quite recently only substituted cyclobutadiene and cyclobutadiene complexes such as LXXVIII were known.[47] As a consequence of the inability to study the parent compound, any statement about the nature of cyclobutadiene drawn by analogy with substituted or complexed cyclobutadienes is at best dissatisfying. The following paragraphs present a brief summary of the chemistry of cyclobutadiene and its derivatives.

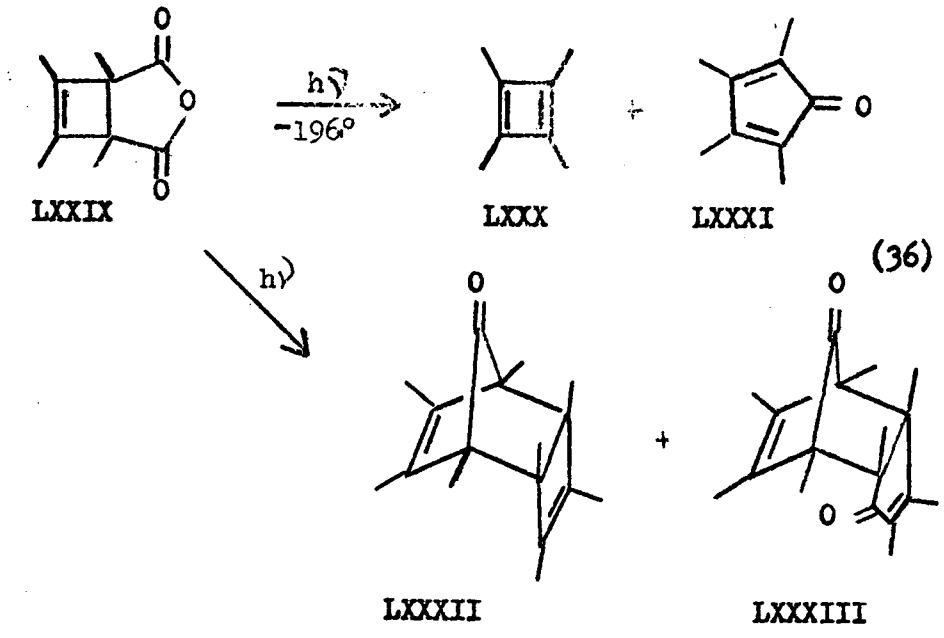


LXXVIII

Since cyclobutadiene would be extremely reactive by all accounts, it is not surprising that special techniques are required

to observe it directly. In fact it is so reactive that the direct observation of even its derivatives offers extreme experimental difficulties.[45] In light of this anticipated reactivity, matix isolation combined with photochemical generation of the species was utilized. Matrix photolysis is a general technique in which the precursor is frozen in an organic glass (e.g., ethanol/hexane in liquid nitrogen) and subsequently photolyzed. Due to the rigidity of the medium, diffusion is prevented and the species of interest can thus be generated in observable quantities if it can be formed.[45]

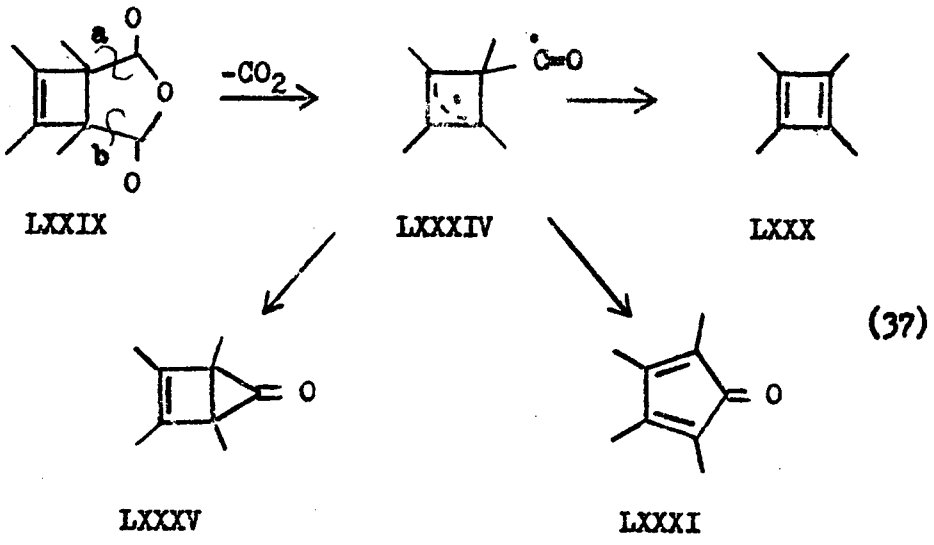
Maier and co-workers have had some success in using cyclobutenedicarboxylic anhydrides as precursors for the photochemical generation of cyclobutadienes. These anhydrides can be prepared by the sensitized photochemical addition of substituted acetylenes to maleic anhydrides. The tetramethyl derivative LXXIX was prepared and photolyzed at room temperature giving a complex mixture of products which have been shown to be derived from intermediates LXXX and LXXXI.[48,49] When LXXIX was photolyzed at -196°, a yellow color was observed which vanished on thawing and Compounds LXXXII and LXXXIII were the only products isolated. Further photolysis of LXXXII and LXXXIII under matrix conditions gave a product mixture identical to that obtained from the room temperature photolysis of LXXIX. It would appear that LXXX and LXXXI are the products of initial formation and that they are trapped in the matrix.



LXXIX LXXX LXXXI

LXXXII LXXXIII (36)

A plausible mechanism for the formation of LXXX and LXXXI is presented below in Equation 37.

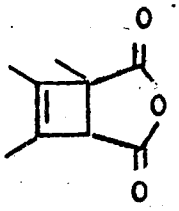


LXXIX LXXXIV LXXX

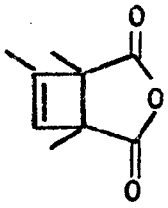
LXXXV LXXXI (37)

Support for this mechanism is provided by the low temperature photolysis of Compounds LXXXVI - a-d.[48-50] When the substituents

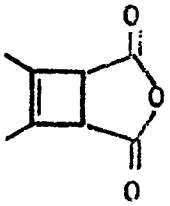
on the anhydride are different, rupture of bond a or b will lead to different diradicals and hence different ketones.



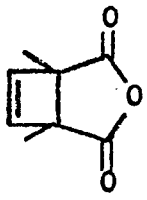
LXXXVIa



LXXXVIb

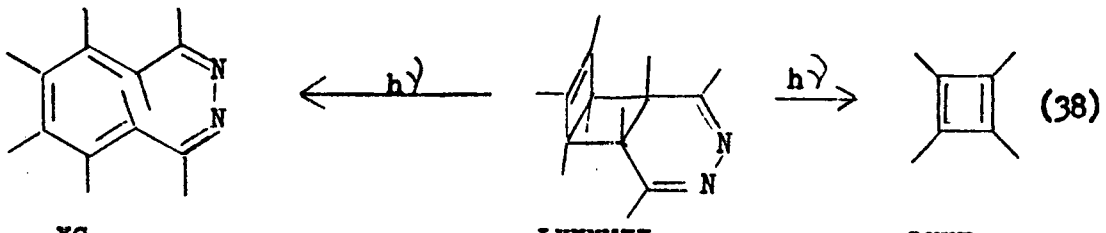


LXXXVIc

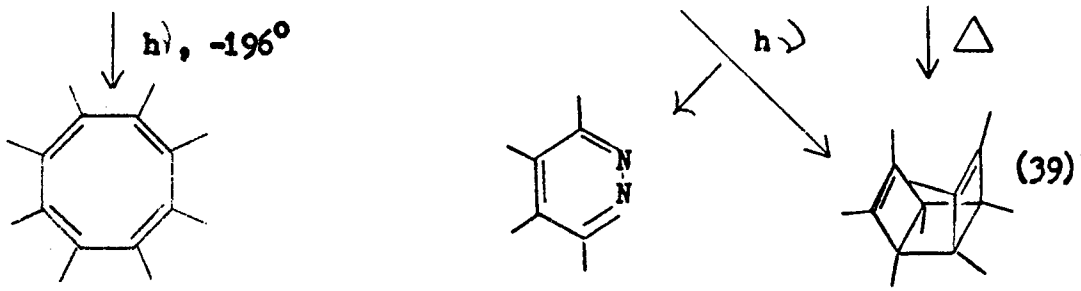


LXXXVId

The yellow color observed in the low temperature photolysis of LXXIX (p 44) is attributed to LXXX (p 44) since photolysis of XC at -196° gave the same yellow color prior to thawing and it is obviously not possible for LXXXI to be present in this case. Further the stereochemistry of the product LXXXVIII clearly indicates the involvement of LXXX (p 44) as an intermediate.[51]

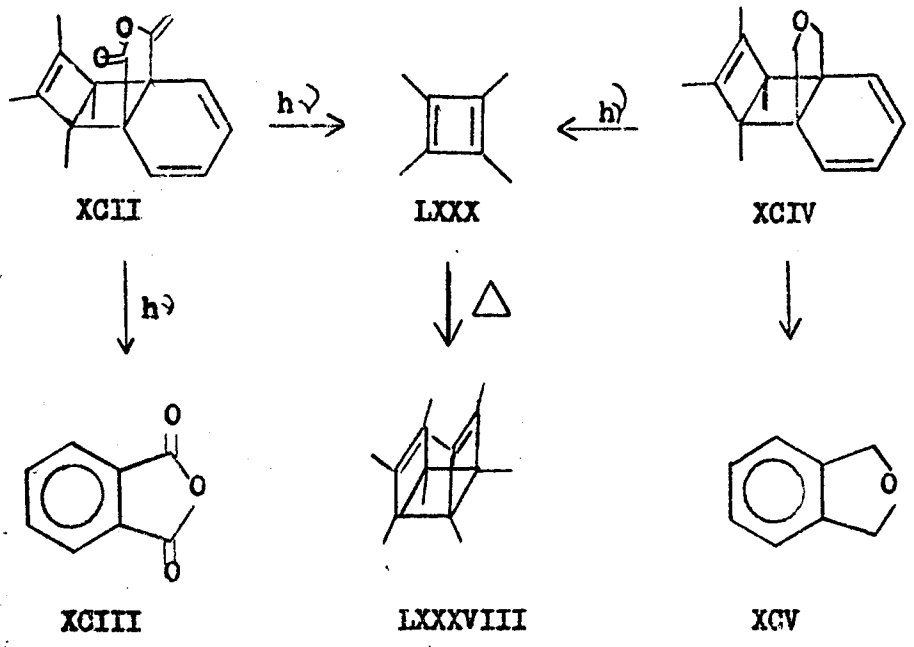


XC LXXXVII LXXX (38)

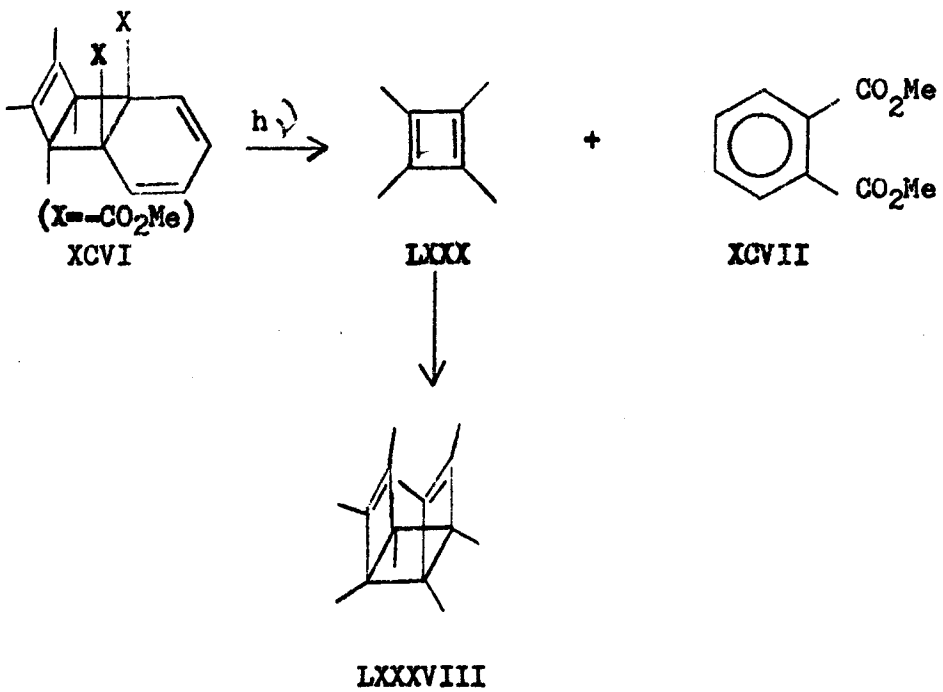


XCI LXXXIX LXXXVIII (39)

Additional evidence for the existence and intermediacy of LXXX (p 44) is provided by the photolyses of XCII, XCIV and XCVI.[52]

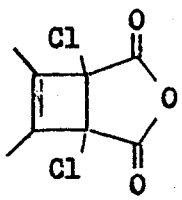


(40)

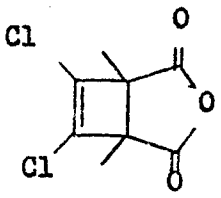


(41)

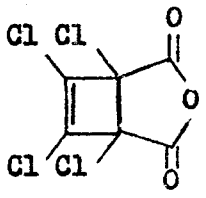
Using Cava's[53] precedent of halogen atoms lending stability to naphthocyclobutadiene, CI, Compounds XCVIII - C, were prepared and photolyzed giving products consistent with the mechanism proposed in Equation 37 (p 44). As would be required by the proposed mechanism, XCVIII and XCIX gave the same adduct of 1,2-dichloro-3,4-dimethylcyclobutadiene to 2,3-dichloro-4,5-dimethyl cyclopentadienone.



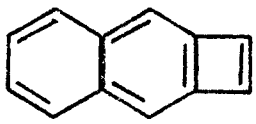
XCVIII



XCIX

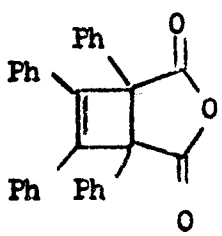


C

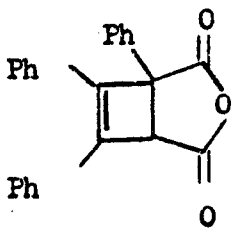


CI

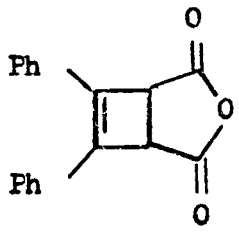
In an attempt to further stabilize cyclobutadiene, the phenyl substituted anhydrides, CII - CIV, were prepared but were found to be too photostable for reaction.[45]



CII

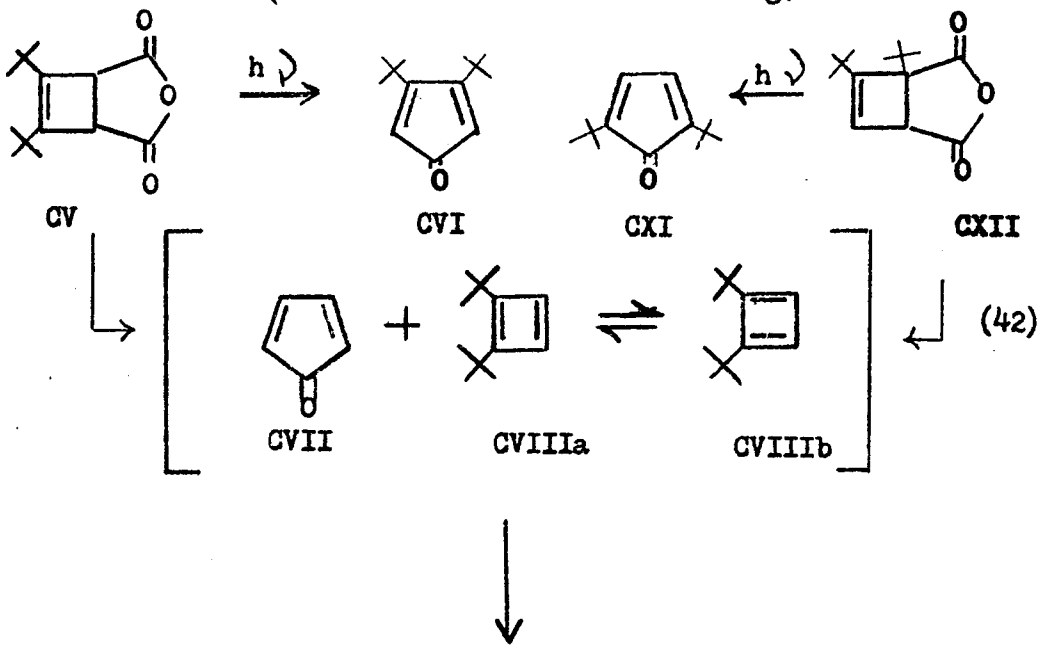


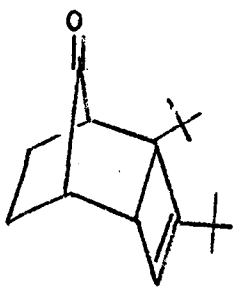
CIII



CIV

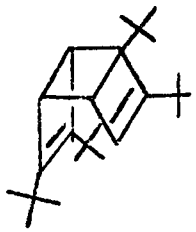
Another approach to a stable cyclobutadiene is to prepare a sterically hindered but electronically intact cyclobutadiene to prevent dimerization or addition products.[54] Compound CV was photolyzed as illustrated in Equation 42. An apparent result of the steric hindrance was the stabilization of CVI to the point where it could be isolated. No dimers of CVI were formed even on heating to room temperature and no addition products with CVIII were observed. Unfortunately, however, this stabilization was not adequate to allow the isolation of CVIII. The isomeric CXII was studied under similar conditions and the ketone CXI was isolated in accordance with the mechanism proposed earlier. Also, Compounds CIX and CX were isolated as would be anticipated. The observed stereochemistry of product CX in both cases indicated that the equilibrium CVIIIa $\rightleftharpoons$ CVIIIb is indeed occurring.[54]





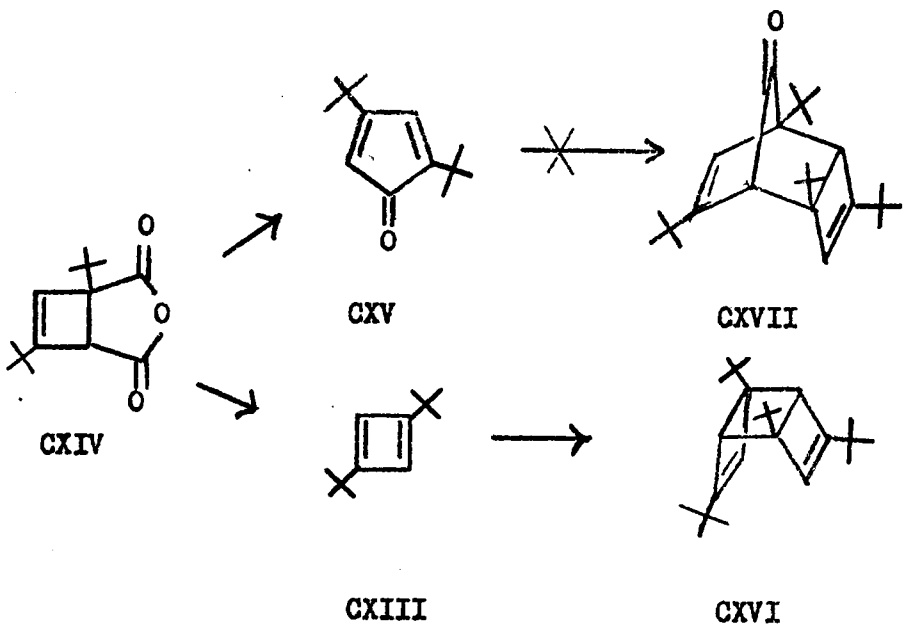
CIX

+



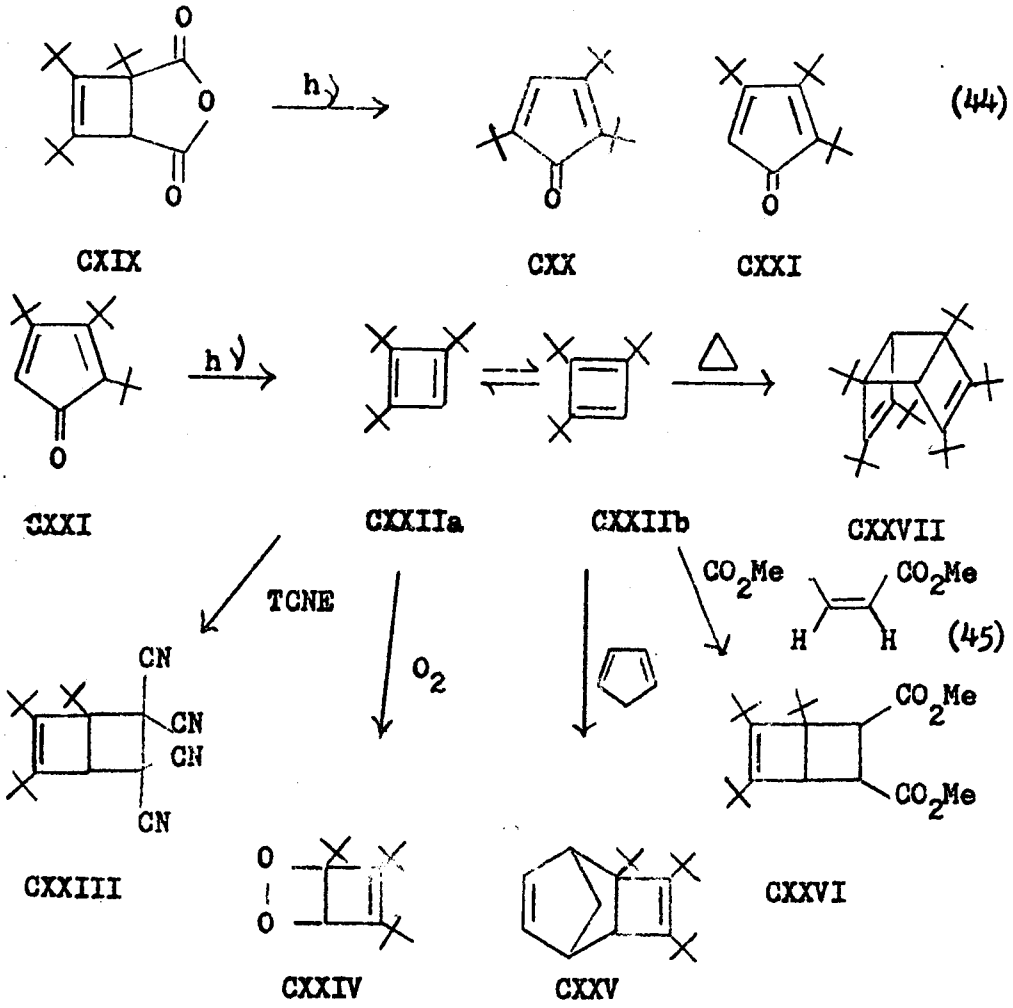
CX

The 1,3-di-tert-butylcyclobutadiene, CXIII, should be even more sterically stabilized than Compound CVIII. This is borne out experimentally by the irradiation of Compound CXIV at -196°C which gives CXV and CXIII as the only products obtained on thawing.[54] In case of Compound CXV the steric stabilization provided by the two tert-butyl groups is sufficient to prevent formation of the Diels-Alder adduct, CXVII, and allows the facile isolation of CXV. However, the stabilization is not sufficiently large to allow the monomer CXIII to be isolated and only the dimer CXVI is obtained on thawing.

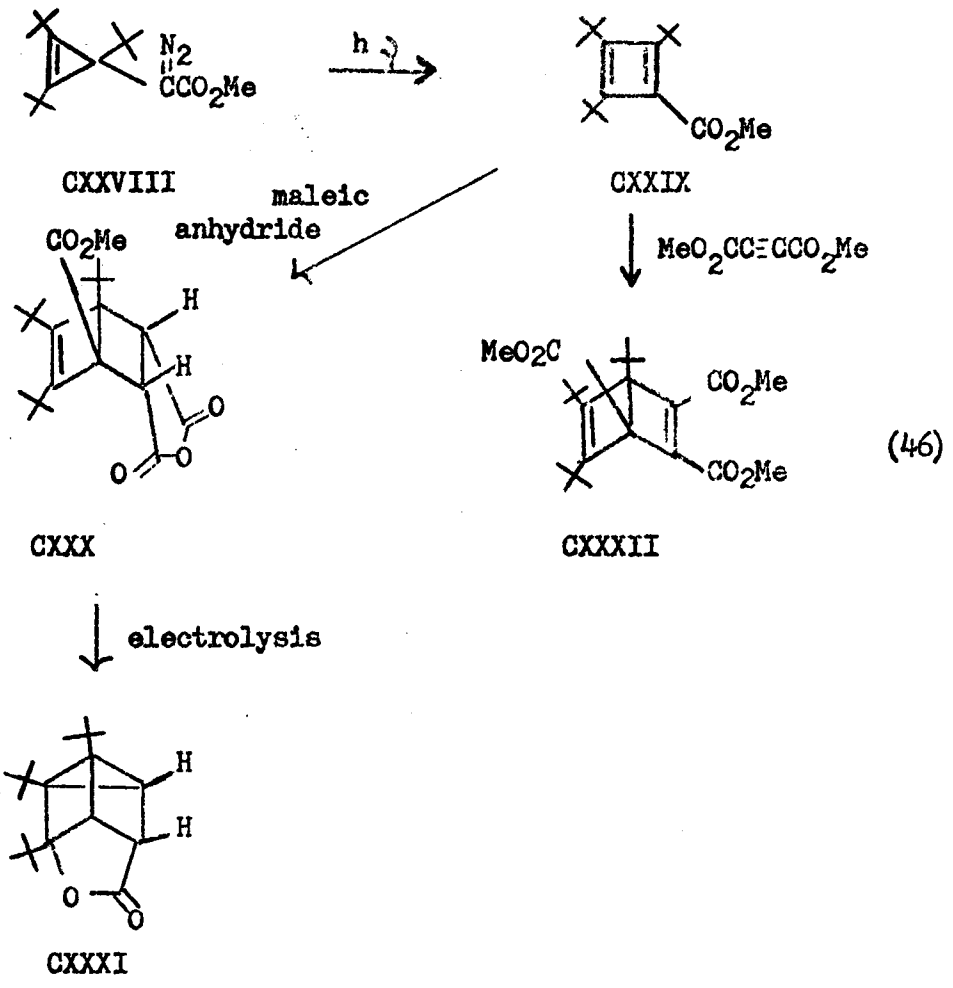


(43)

If the above reasoning is valid, tri-tert-butylcyclobutadiene, CXVIII would be stabilized further and might be isolated as the monomer. Unfortunately, photolysis of CXIX gives only the cyclopentadienones, CXX and CXXI and no CXVIII or dimer. Further study showed Compound CXX to be photostable at all temperatures. However, CXXI, while photostable at room temperature, is photocleaved at -196°C losing CO (ir) to form CXXII (nmr) which survives thawing but completely forms the dimeric product, CXXVII, on standing 24 hr. Nmr studies of CXXII showed that the two tert-butyl groups adjacent to the ring proton to be equivalent thereby providing evidence, for the equilibrium existence between CXXIIa and CXXIIb. Further evidence for the existence of CXXII is provided by the formation of cycloeddition products with cyclopentadiene, dimethyl maleate, tetracyanoethylene and oxygen as illustrated in Equation 45.



Masamune, et al.,[7] were able to prepare tri-tert-cyclobutadienes by independent routes as shown in Equation 46.

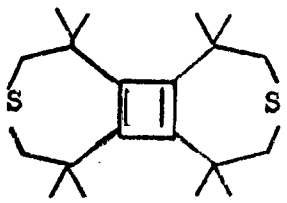


(46)

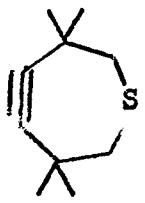
Compound CXXIX is a stable crystalline solid which gave the cycloaddition products CXXX and CXXXII on reaction with maleic anhydride and dimethyl acetylenedicarboxylate, respectively. In a similar manner Masamune and co-workers were able to prepare Compound CXXII (p 51) which, while similar in behavior to Compound CXXIX, was much more reactive.

While it would appear that tetra-<u>tert</u>-butylcyclobutadiene should be even more stable than Compound CXXII (p 51) it has not proven possible to prepare the necessary starting anhydride.[45]

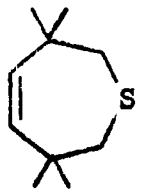
Krebs and co-workers recently prepared the stable cyclobutadiene derivative CXXXIII.[55,56] In contrast to the donor-acceptor cyclobutadiene such as the iron tricarbonyl complexes, Compound CXXXIII has a cyclic-conjugated π-system. Further CXXXIII contains a [4]-annulene system which is apparently not affected by the presence of the two sulfur atoms as evidenced by the good agreement between the n-sulfur ionizations in Compounds CXXXIII and CXXXV. Because no transannular n/π interactions were observed in Compound CXXXIV none would be expected in CXXXIII and the use of CXXXIII as an approach to the study of cyclobutadiene itself is apparently valid.



CXXXIII



CXXXIV



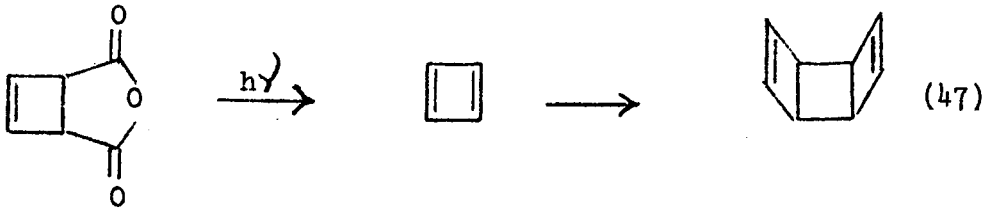
CXXXV

Compound CXXXIII was shown to have a ground state singlet by the comparison of calculated ion energies with ion energies obtained by photoelectron spectroscopy. If the ground state were a triplet, there would have been two π-ionizations observed in the region of lower ionization potentials. Experimentally only one π-ionization was observed in this region in accord with calculations

for the singlet. In addition it was discovered that the triplet was not detectably occupied even at elevated temperature (110°).

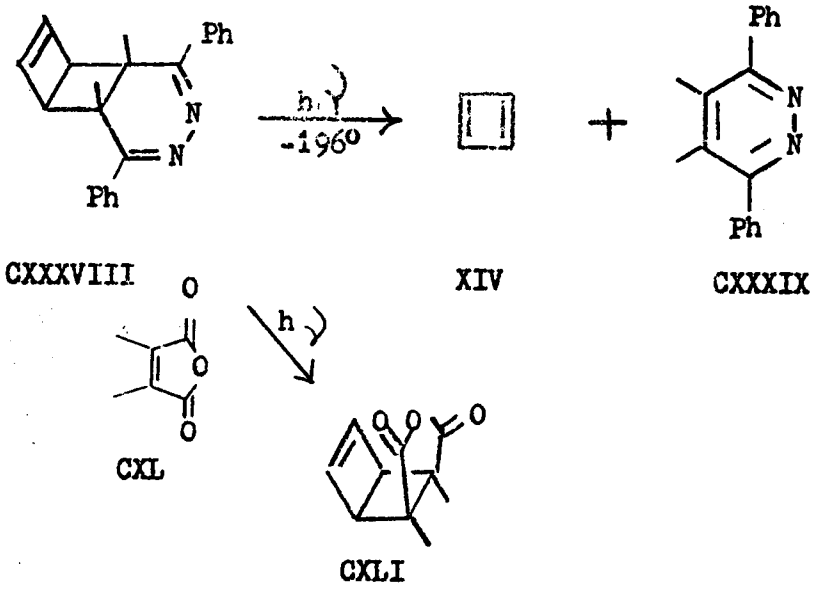
In spite of the success in isolating Compound CXXII (p 51) which does have its electronic structure intact, preparation and direct observation of the parent compound, XIV (p 12) would be much more satisfying. Nenitzescu and co-workers have demonstrated that Compound XIV (p 12) is an intermediate in the dehalogenation of 3,4-dichlorocyclobutene.[57] Further, Pettit and co-workers[36] have shown XIV (p 12) to be an intermediate in the oxidative decomposition of the iron carbonyl complex of cyclobutadiene, LXXVIII (p 42).

In the search for a satisfactory route the low temperature photolysis of the cyclobutenedicarboxylic anhyrdride, CXXXVI should be investigated. Unfortunately its ultraviolet absorption (λ_{max} = 2280Å, ϵ = 670) made photolysis difficult. Room temperature irradiation gave only the dimeric product, CXXXVII. Matrix photolysis gave low conversion to a product which has a uv band at 3010Å assignable to XIV (p 12). This is supported by the isolation of Compound XCCCVII from the low temperature photolysis of CXXXVIII. Room temperature photolysis of CXXXVIII in the presence of excess dimethyl maleic anhydride gave CXLI.[58]



(47)

CXXXVI XIV CXXXVII

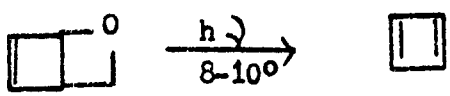


CXXXVIII XIV CXXXIX

CXL CXLI

(48)

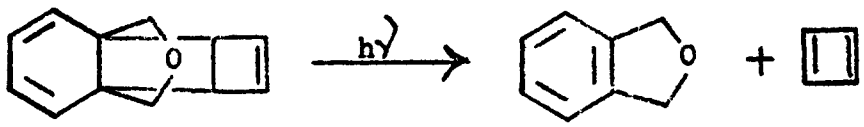
Chapman's[59] and Krantz'[60] group have generated XIV (p 12) from CXLII in a noble gas matrix at 8-20°. It was possible to identify XIV (p 12) by its ir spectrum which is compatible only with a square planar structure. In addition, Masamune[61] generated Compound XIV (p 12) in the same manner and was unable to observe any esr signal due to a triplet.



CXLII XIV

(49)

Masamune's group prepared XIV (p 12) according to Equation 50. They obtained a species XIV (p 12) having a uv maximum at 300-305 nm in agreement with Maier's observation for XIV (p 12). They were unable to observe any esr signal in the matrix attributable to a ground state triplet of XIV (p 12).

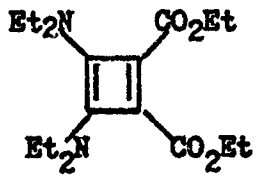


(50)

CXLIII CXLIV XIV

In conclusion there is some physical evidence in favor of a ground state singlet for cyclobutadiene. As stated earlier all attempts to observe an esr signal indicative of a ground state triplet in matrices of XIV (p 12) have failed. This failure to observe a signal can only be considered negative evidence. However, there is a chemical argument for a singlet cyclobutadiene. When cyclobutadienes dimerize there is the possibility of forming both <u>syn</u> and <u>anti</u> adducts. Thus far only <u>syn</u> products such as CX (p 49) and CXXXVII (p 54) have been isolated from the matrices on thawing. This result is in accord with the endo rule commonly observed for Diels-Alder reactions and thus favors the singlet. This conclusion relies of course on the assumption that only the singlet can be stereospecific; however, there is no experimental proof that a triplet could not also be stereospecific. The ir data for XIV (p 12) provide some confusion. The data are compatible

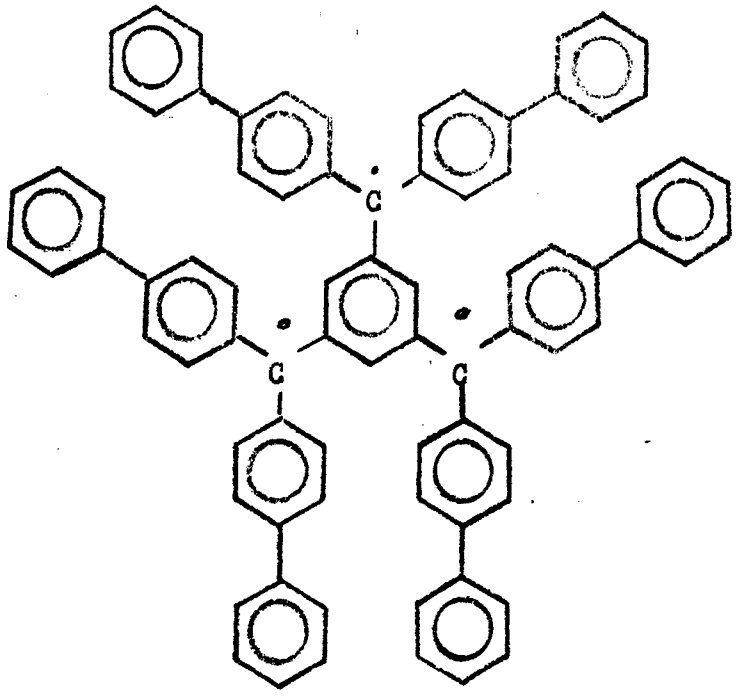
only with a square geometry or that required for a ground state triplet. Also why do the uv spectra of cyclobutadiene differ vastly from uv spectra of more highly substituted derivatives such as CXLV which was investigated by Gompper and co-workers in an attempt to study cyclobutadiene in spite of that molecule's fleeting existence.[62]



CXLV

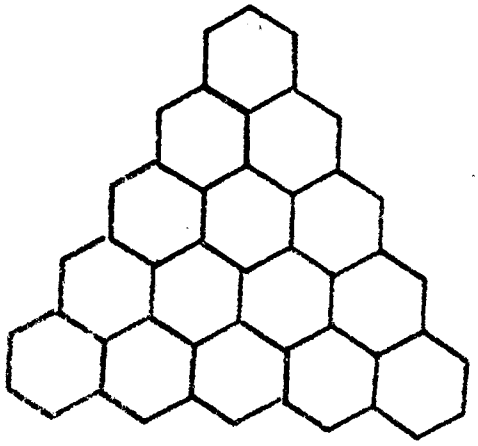
C. High Spin Systems

Obviously spin multiplicity is not limited to the singlets, doublets and triplets described in the previous pages. Kothe and Zimmermann have recently reported the observation of molecule CXLVI possessing a ground state quartet, CXLVI. Hückel theory and Hund's rules combine to require $s = 3/2$; hence, $m_s = 2s+1 = 4$ or a ground state quartet as observed.[63]



CXLVI

The following system, CXLVII, in which each carbon atom has one unpaired electron and one p orbital should have a ground state quintet although it has not been prepared.[64]



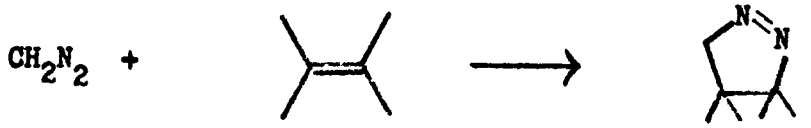
CXLVII

D. Cyclic Azo Decompositions

In the recent literature the decomposition of cyclic azo compounds has been shown to be a highly useful route to interesting organic molecules as well as an extremely successful means of generating unstable intermediates for mechanistic studies.

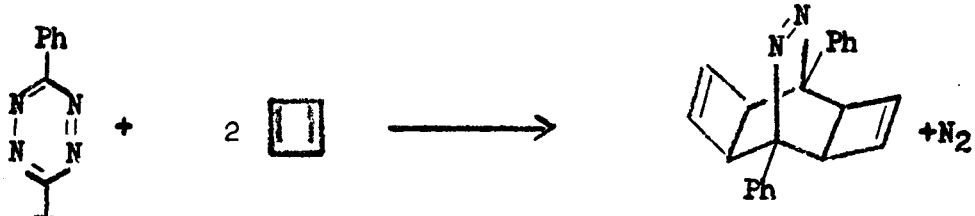
1. Formation of Cyclic Azo Compounds

A direct synthetic route to cyclic azo compounds is provided by the cycloaddition of diazomethane to olefins.[65,66]

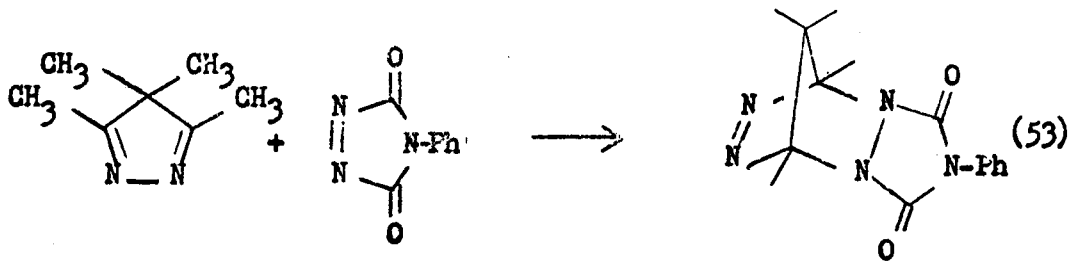


XXXIII CXLVIII CXLIX (51)

A second direct route is the reaction of substituted s-tetrazines, 3,4-diazonorcaradienes and isopyrazoles with active dienophiles.[67,68]



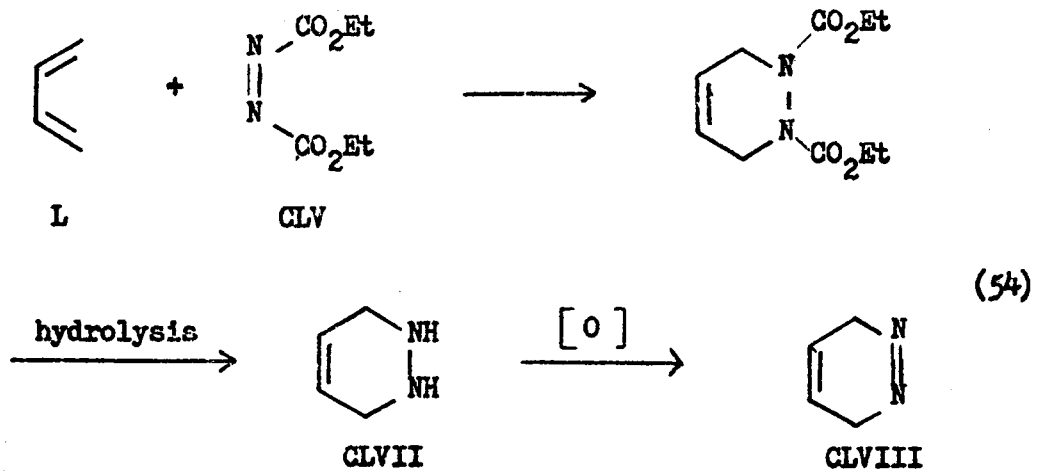
CL XIV CLI (52)



(53)

CLII CLIII CLIV

Perhaps the most common method of generating cyclic azo compounds is the cycloaddition of a reactive diene to an azo compound, e.g., diethyl azodicarboxylate or N-phenyl triazoline-3,5-dione, followed by hydrolysis and oxidation as shown in Equation 54.[69]



(54)

L CLV CLVII CLVIII

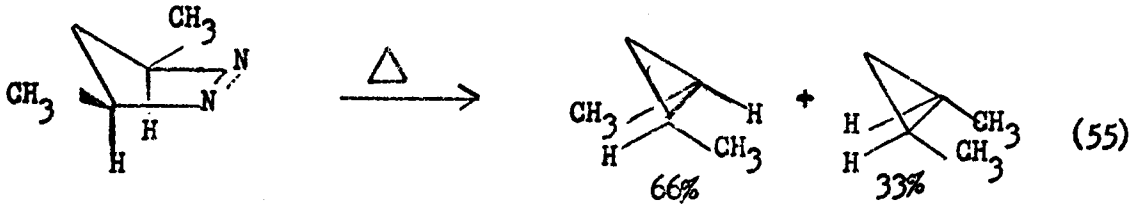
Obviously additional chemical modifications can be carried out on the intermediates thereby enhancing the utility of the procedure. The hydrolysis step can be either acidic or basic although the use of base is more common. Oxidation can be carried out using a variety of reagents such as mercuric oxide, cupric chloride, silver oxide, nitric acid, hypochlorous acid and air. Mercuric chloride is the reagent of choice since this heterogeneous oxidation can be used with a wide variety of solvents and on completion of the reaction excess mercuric oxide and mercury can be removed by filtration. It should be noted that cupric chloride can be used to oxidize the hydrazine in cases where unstable azo intermediates are formed. The hydrazine is oxidized by cupric chloride to give a stable crystalline complex which can then be used to generate the desired azo compound by treatment with base.[70]

2. Mechanism and Stereochemistry of Decomposition of Cyclic Azo Compounds

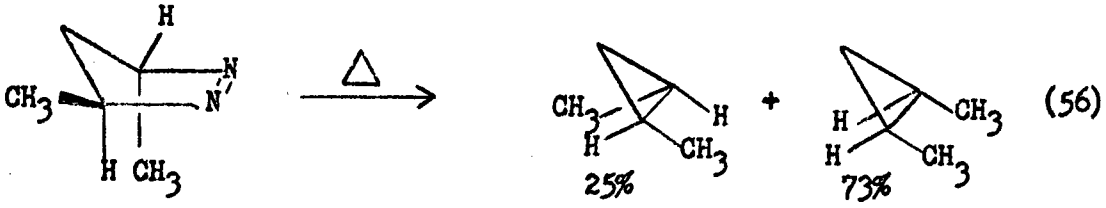
Cyclic azo compounds are known to decompose by a variety of subtly controlled mechanisms which are accompanied by widely varying stereochemical results. The following discussion is an attempt to summarize those decomposition pathways and the pertinent experimental data supporting them.

Crawford *et al.*[71,72] have carried out a comprehensive investigation of the pyrolysis of 1-pyrazolines. This pyrolysis is a potential route to trimethylene — a species which is predicted to be a ground state triplet if the p orbitals are parallel.[4]

Using appropriate stereochemical labels, the major decomposition pathway was found to result in a product having a single stereochemical inversion as illustrated in Equations 55 and 56.



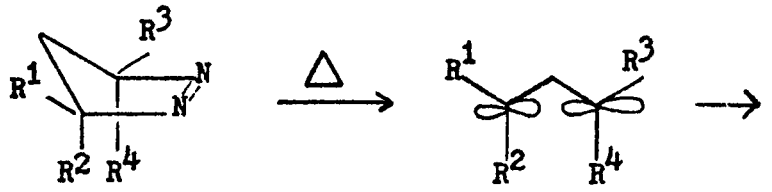
CLIX CLX CLXI (55)



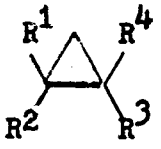
CLXII CLX CLXI (56)

As used here single inversion in the product refers to the inversion of the stereochemistry about only one of the carbon atoms initially bonded to nitrogen. A plausible mechanism, which is favored by Crawford and Mishra,[71] is the direct formation of the diradical intermediate which then undergoes predominant conrotatory ring closure (Equation 57) thereby giving experimental support to Woodward and Hoffman's theoretical treatment of pericyclic reactions. The experimentally determined entropies for the reaction described in Equation 57 for a wide variety of substituents are in general small and positive as would be anticipated for a concerted process and

thus lends some support to this mechanism. The entropies of activation (250°C) observed for the dimethyl-1-pyrazolines of structure CLXIII are of the order of 9±1eu. In general the more negative the entropy the more ordered or concerted the transition state is assumed to be. Hence the magnitude of the entropy of activation is frequently used as a measure of "concertedness" for a given reaction. Entropies of activation for non-concerted azo decompositions are typically of the order of +30eu (250°C).

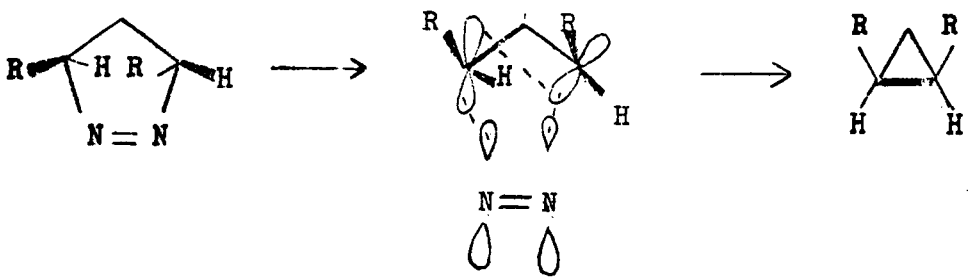


CLXIII CLXIV



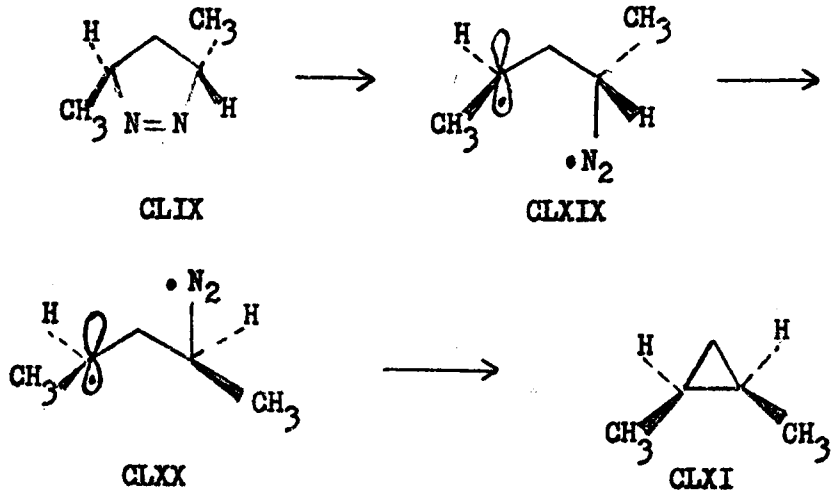
CLXL (57)

An alternate explanation which might be considered is a symmetry-allowed one-step reverse 2+2 reaction. More specifically the allowed $[\sigma 2_a + \sigma 2_s]$ (shown in Equation 58) would generate the required products.



CLXVI CLXVII CLXVIII (58)

Another equally plausible and difficult to disprove mechanism is the cleavage of one C-N bond followed by the radical center of CLXIX carrying out a backside displacement of N_2 at C-4 again producing the observed stereochemistry (Equation 59).[84]

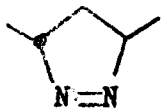


(59)

In order to substantiate their proposed mechanism, Crawford and Mishra[71] used stereochemical and kinetic isotope methods. Compounds CLXXI - CLXXIV, CLIX and CLXII were prepared and the pyrolyses studied kinetically. Both CLIX and CLXII were found to have an E_a lower than that of CLXXII, CLXXIII and CLXXIV. This provides support for a concerted mechanism involving simultaneous C-N bond cleavage.

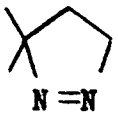

CLXXI


CLIX


CLXII


CLXXII

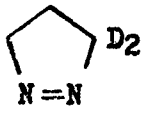

CLXXIII


CLXXIV

Compounds CLXXV, CLXXVd_2 and CLXXVd_4 were prepared and their gas phase kinetics studied. These kinetic ratios indicate quite strongly that simultaneous C-N bond cleavage is occurring, since the approximately equal additive isotope effects indicate that both N-C bonds are involved.


CLXXV


CLXXV-d_2

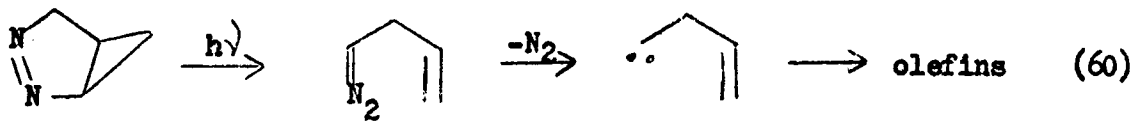

CLXXV-d_4

k_H/k_D	1.19	1.40

Thus in the case of simple 1-pyrazolines the mode of thermal decomposition appears to be via a concerted loss of nitrogen followed by predominant conrotatory ring closure of the resulting trimethylene diradical in Crawford's opinion. However, some recent observations by Takagi and Crawford[72] on the thermal decomposition of a number of mono- and diolefinic azo compounds have led Crawford to state that these reactions at least involve sequential

carbon-nitrogen bond cleavage in the rate determining step. Additional experimental work is presently under way by Crawford and co-workers to determine conclusively the mode of nitrogen elimination in the cyclic azo decomposition.

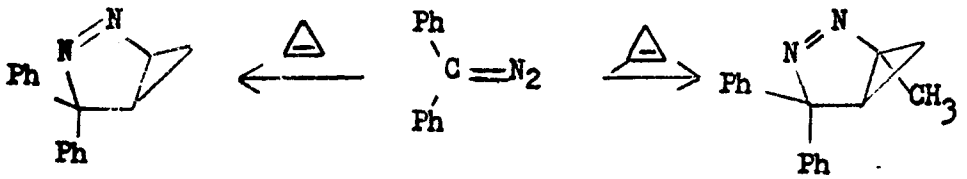
A demonstration of how the mechanism of cyclic azo decomposition can be changed by seemingly minor changes is shown in recent contrasting papers by Eaton, Bergman and Hammond[73] and Gassman and Greenlee.[74] Hammond, et al., demonstrated that the photochemical decomposition of CLXXVI occurs via a carbene intermediate which then gives olefinic products as seen in Equation 60.



(60)

CLXXVI CLXXVII CLXXVIII

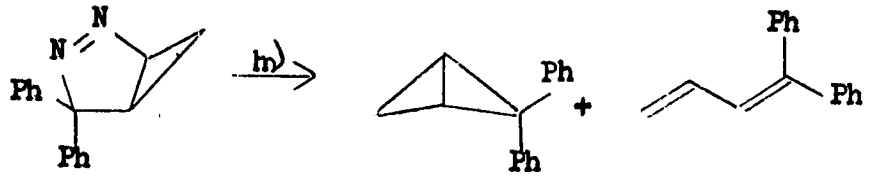
In contrast, Gassman and Greenlee[74] have shown the presence of phenyl substituents to alter the mechanism significantly. The compounds chosen for study were CLXXIX and CLXXXI which were prepared as shown in Equation 61.



(61)

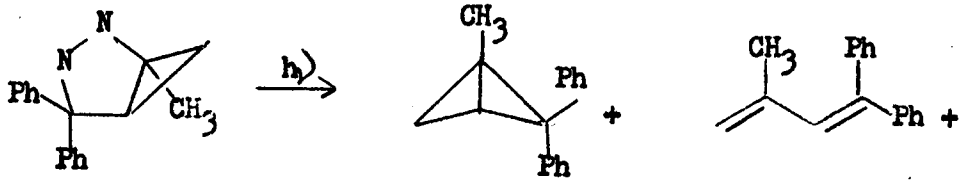
CLXXIX CLXXX CLXXXI

The photochemical decompositions of CLXXIX and CLXXXI are summarized below (Equations 62 and 63).



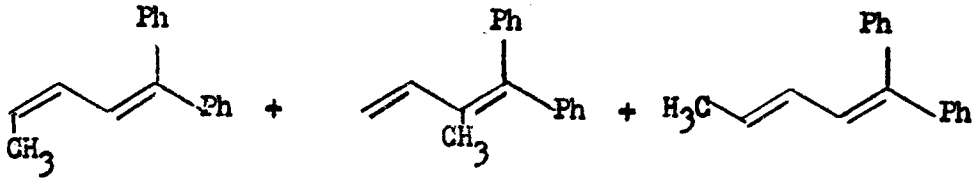
(62)

CLXXIX CLXXXII CLXXXII



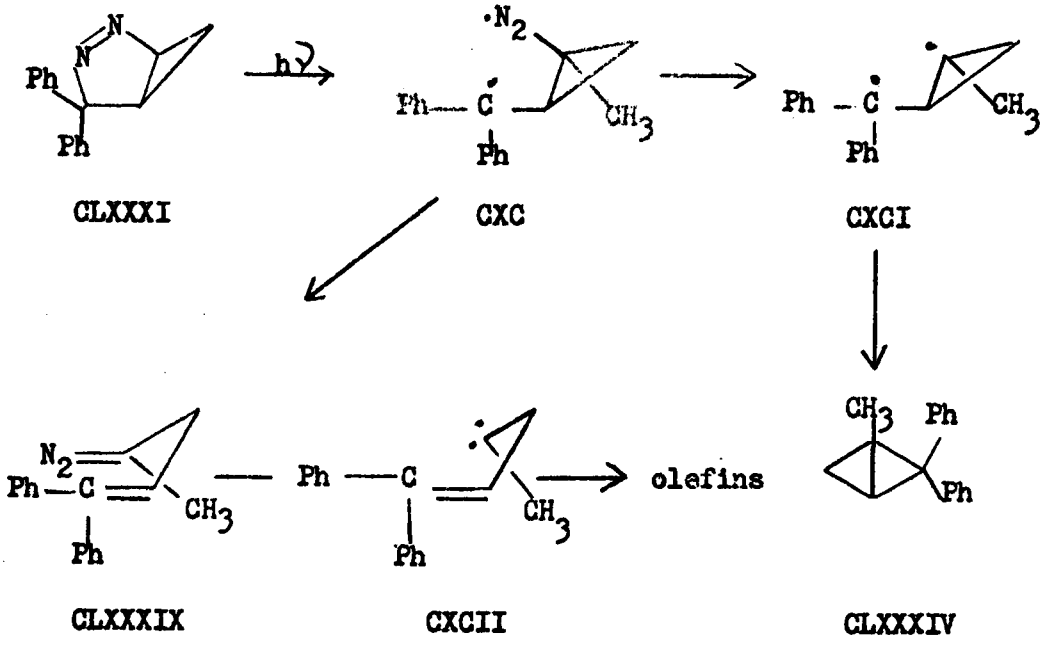
(63)

CLXXXI CLXXXIV CLXXXV



CLXXXVI CLXXXVII CLXXXVIII

The presence of the bicyclobutane appeared to require a modification of Hammond's mechanism. In a careful nmr study of the photolysis of CLXXXI, it was found that CLXXXIV and CLXXXIX were the initial products. Compound CLXXXIX then formed a carbene which subsequently formed the observed olefins.[74]

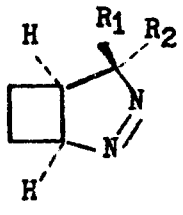


CLXXXI CXC CXCI

(64)

CLXXXIX CXCII CLXXXIV

White, Condit and Bergman[75] have studied the thermal decomposition of a number of cyclic azo compounds having the general structure defined by CXCIII. In the case of the parent compound (R_1=R_2=H), the decomposition was found to proceed by two parallel paths. The first path is a carbene route which leads to 1,4-dienes and olefinic products and the second is a diradical route leading to bicyclopentanes and cyclobutanes.



CXCIII

Unfortunately in this case it was not possible to determine whether the carbene was generated directly or if it was formed by ring cleavage and subsequent nitrogen loss. In order to elucidate the mechanism pure CXCIVe and CXCIVn were prepared and their pyrolytic behavior studied. Figure 3 summarizes the results. Product CXCVII completely retains the stereochemistry of the starting compound thereby indicating that it is formed from CXCIV by a retro-1,3-dipolar addition instead of by ring cleavage of CXCIX which would be expected to randomize. However, the other carbene product, the vinylcyclopropane CCI, does have some stereorandomization indicating that it is formed by both pathways. The bicyclopentane products, CCII and CCIII, offer the most information in that with both the endo and exo pyrazoline, predominant single inversion was involved. The product ratios for CCII and CCIII are similar to those obtained by Crawford, et al.[71] in their study of CLIX (p 62) and CLXII (p 62) as discussed earlier (p 62).

Crawford and Mishra's explanation of the similar predominant singlet inversion in the pyrolyses of alkyl substituted 1-pyrazolines invoked a π-cyclopropane intermediate which then underwent conrotatory ring closure. If this is indeed the case it must be energetically close to a process which is less selective since some double inversion and double retention products were also observed.

It is therefore most intriguing that the introduction of a two carbon bridge as in CXCIVe (which should certainly introduce

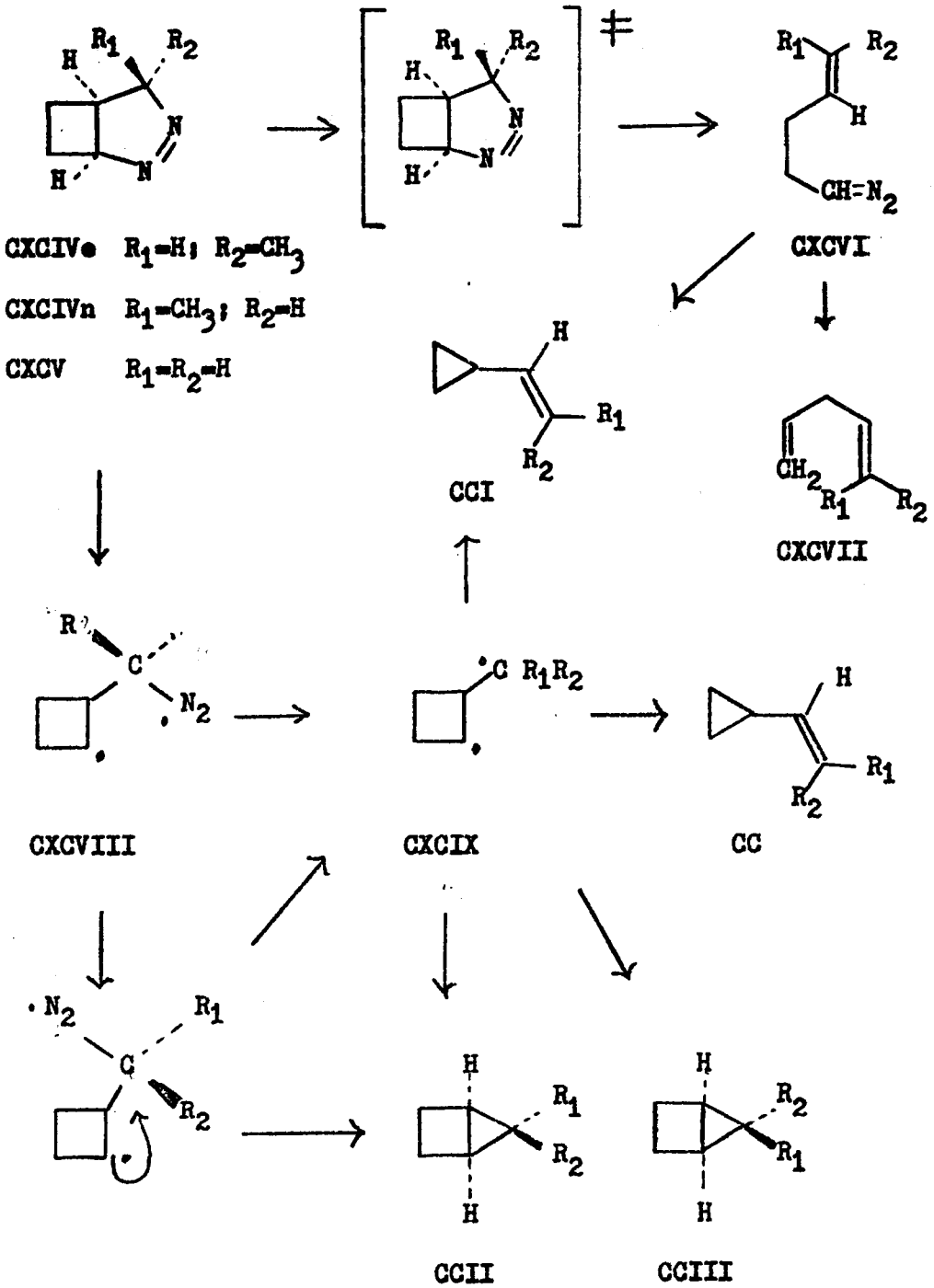
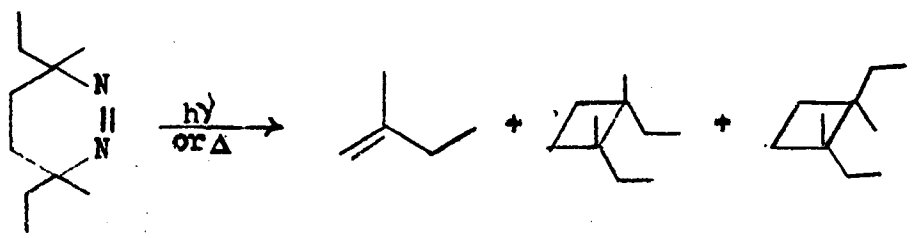


Figure 3. Mechanism for the thermal decomposition of 2,3-diazabicyclo [3.2.0] hept-2-enes.

strain into the 0,0 intermediate thereby making the secondary path more important) does not signifigantly alter the CCII/CCIII ratio. This absence certainly provides evidence against the 0,0 diradical. The term "0,0" was introduced by Hoffmann[76] and refers to the conformation of trimethylene having both of the terminal methylene groups in the C-C-C plane. The term "90,90" refers to the conformation having the methylene groups perpendicular to the C-C-C plane. Finally, "0,90" refers to the conformation having one methylene in the C-C-C plane and the other perpendicular to the plane. Figure 2 (p 70) illustrated Bergman's[75] alternate and previously described backside displacement of nitrogen mechanism.

In contrast to the 1-pyrazolines where single inversion predominated, Bartlett and Porter[77] have studied the thermal and photochemical decomposition of meso- and d,l- CCIV finding that the thermal and unsensitized photochemical reactions proceed with predominant retention of configuration as shown in Table I presumably through a singlet intermediate.



(65)

CCIV CCV CCVI CCVII

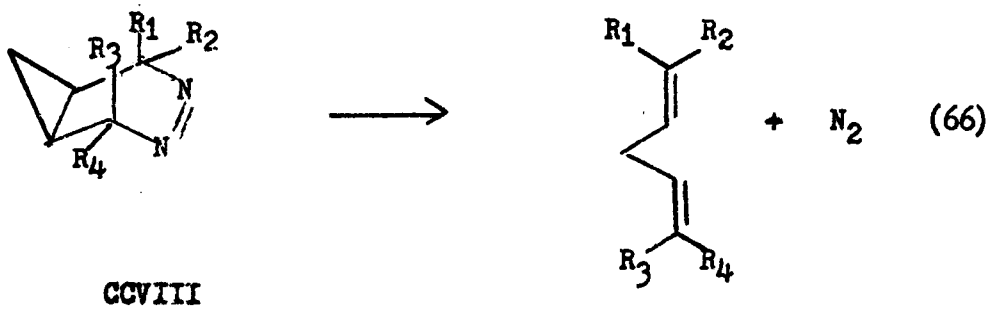
TABLE I

Product Distributions for Decompositions of Compound CCIV (p 71)

Isomer	Mode of Decomposition	% CCV	% CCVI	% CCVII	% Retention in CCVI and CCVII
meso	△	49	43	2.5	98
d,l	△	51	3.5	42	98
meso	hν	61	35	3.5	95
d,l	hν	60	4	33	97
meso	hν, thioxanthane	77	11.5	8	61
d,l	hν	75	8	12	65

When the photolysis is sensitized by thioxanthone, the percentage of retention drops from 95% of retention of configuration to 65% and the percentage of cleavage product goes up considerably. This behavior can be explained in terms of a relatively long-lived triplet diradical produced by the sensitization. The parallel spins of the triplet biradical would tend to delay ring closure; spin inversion would be necessary before bond formation could occur. This would cause an increase in the amount of cleavage to CCV as is observed. Further, the relative long life of the triplet species will allow rotation about all three C-C single bonds to proceed to a much greater extent than would be expected from the singlet and the amount of retention is greatly reduced.

In the recent literature Berson, et al.,[78] have studied the thermal decomposition of a series of diazabicyclo[4.2.0]octenes. They had previously demonstrated that the thermal decomposition of compounds CCVIII a-c were concerted cycloreversions.



(66)

CCVIII

a. R_1, R_3=CH_3; R_2, R_4=H

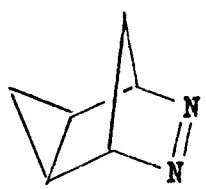
b. R_1, R_4=CH_3; R_2, R_3=H

c. R_1, R_3=H; R_2, R_4=CH_3

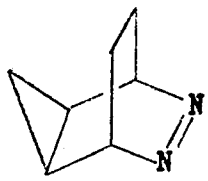
The facts supporting a concerted mechanism in this case are the following:

1. Nitrogen was evolved at a rate greater than would be expected from simple models.
2. There were no products of ring closure.
3. High stereospecificity and adherence to the allowed pathway having the best overlap of the orbitals undergoing bond cleavage.

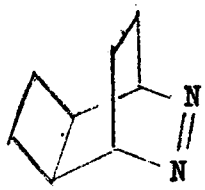
Allred, Hinshaw and Johnson[79] have observed similar behavior for CCX - CCXII and a concerted mechanism has been assigned for the thermal decomposition. However, Compound CCXII appears to be a borderline case as it decomposes much more slowly than the cyclopropyl analog and does give ring closure product.



CCX



CCXI



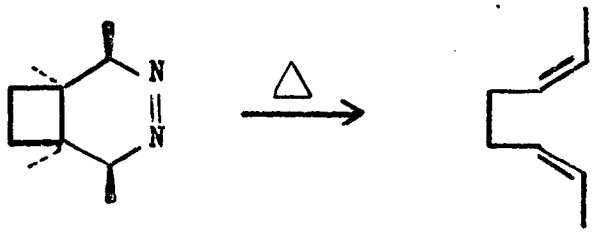
CCXII

With these results at hand, Berson[78] sought to determine the criteria for a concerted versus non-concerted mechanism. Going from a cycloproply ring in CCXI to a cyclobutyl ring in CCXII reduces the bent character of the bridge bond and thereby weakens the overlap with the two breaking carbon-nitrogen bond orbitals in the concerted transition state. The net result would be the

narrowing of the energy gap between concerted paths as well as the energy gap between concerted and non-concerted pathways.

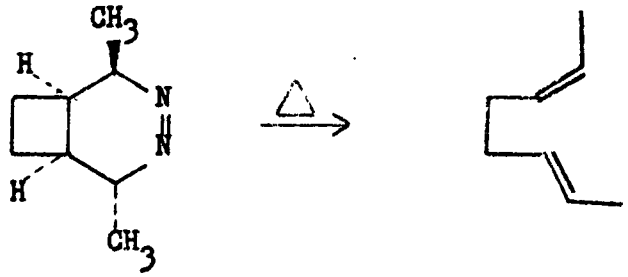
Berson et al.[78] were able to prepare pure samples of CCXIII and CCXV which were then pyrolyzed. The hydrocarbon products were CCXIV and CCXVI respectively.

No products of ring closure were observed and the hydrocarbons were demonstrated to be direct products of decomposition having stereospecificities of greater than 99.9%. On a relative scale CCXIII and CCXV lose nitrogen at a rate approximately five times faster than Allred's Compound CCXII (p 74) but slower than CCVIIIa-c (p 73). This rate decrease observed in Compounds CCXIII and CCXV may be explained as a result of reduced bent character in the bridge bond. As a result the stereospecificity could be expected to be less than that for CCVIIIa-c (p 73); however, it is still beyond the limits of detection.



(67)

CCXIII CCXIV



(68)

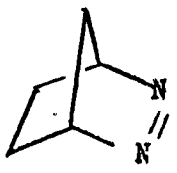
CCXV CCXVI

Allred and Johnson[70] recently reported that Compound CCX (p 74) decomposed 10^{11} times faster than CCXVII. Compound CCX (p 74) also demonstrated to decompose in a concerted manner. In an effort to elucidate the factors responsible for this remarkably accelerated rate of decomposition Compounds CCXVIII, CCXX and CCXXII were prepared. These compounds were pyrolyzed and their kinetic parameters were determined (Table II). The large negative $\Delta S^{\ddagger}$ and relatively low E_a indicate a concerted mechanism for CCXX and CCXXII while the large positive S and high E_a for CCXVII (p 74), and CCXVIII indicate a biradical pathway for these compounds. The simplest explanation for the difference in rates for Compounds CCXVIII, CCXX and CCXXII lies in the strain in the transition state. In a concerted pathway the one carbon bridge at C_5 would cause strain as C_1, C_2, C_3, and C_7 rehybridized to give CCXIX. This effect is relieved by the two carbon bridge in compound CCXX and still more in CCXXII. Also the orientation of the cyclopropyl ring is more favorable for orbital overlap in CCXX and CCXXII.

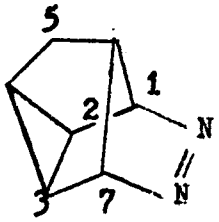
TABLE II

Thermolysis Rate Data for Some Azo Compounds

Compound	Temp, °C	10^4k, sec^{-1}	E_a, kcal/mole	$\Delta S^{\ddagger}$, eu	Rel rate
CCXVII	+180.8	8.35	37.3 ± 0.3	+ 8.7	
	- 3.5				1
CCX	- 3.5	1.04	17.3 ± 1.6	-13	2.2×10^{11}
CCXVIII	+150.0	2.33	36.3 ± 0.3	+ 8.3	
	- 3.5	4.34×10^{-11}			9.2
CCXX	+ 50.0	3.31	23.3 ± 0.4	- 5	
	- 3.5	2.46×10^{-3}			5.2×10^{8}
CCXXII	- 3.5	0.90	19.6 ± 0.9	- 6	1.9×10^{11}



CCXVII



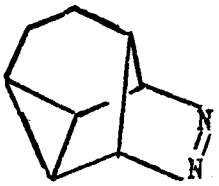
CCXVIII

$\xrightarrow{\Delta}$



CCXIX

$+ N_2$ (69)



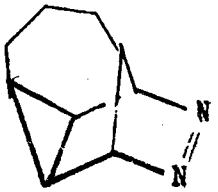
CCXX

$\xrightarrow{\Delta}$



CCXXI

$+ N_2$ (70)



CCXXII

$\xrightarrow{\Delta}$

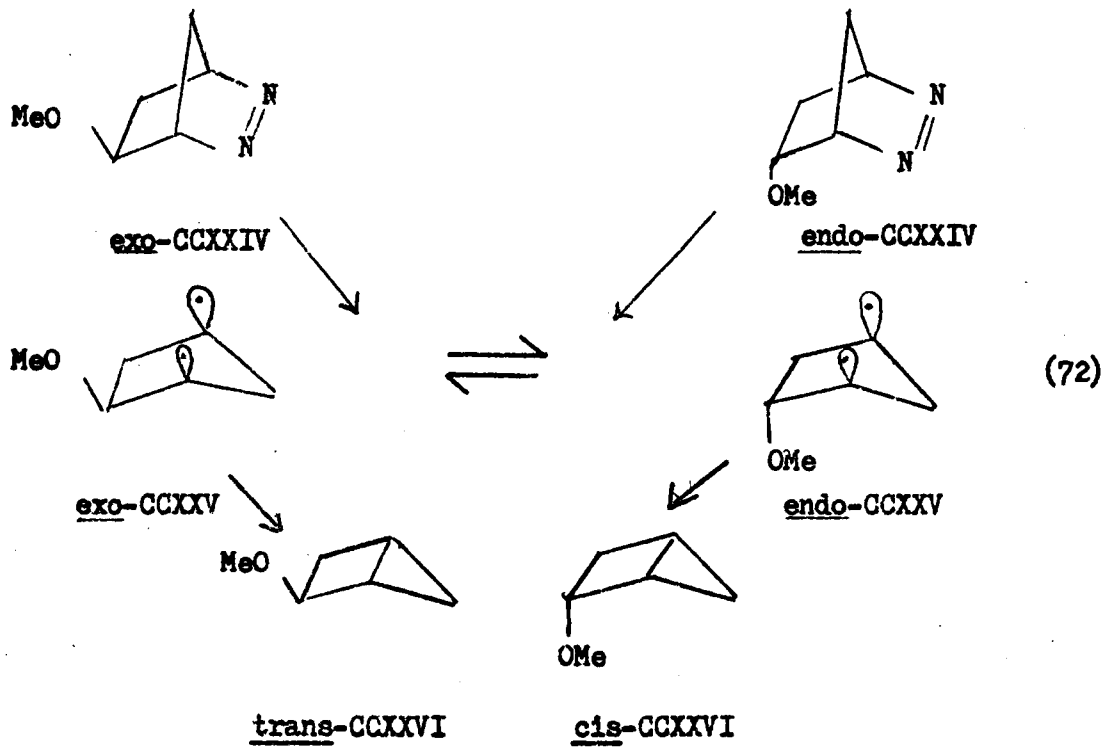


CCXXIII

$+ N_2$ (71)

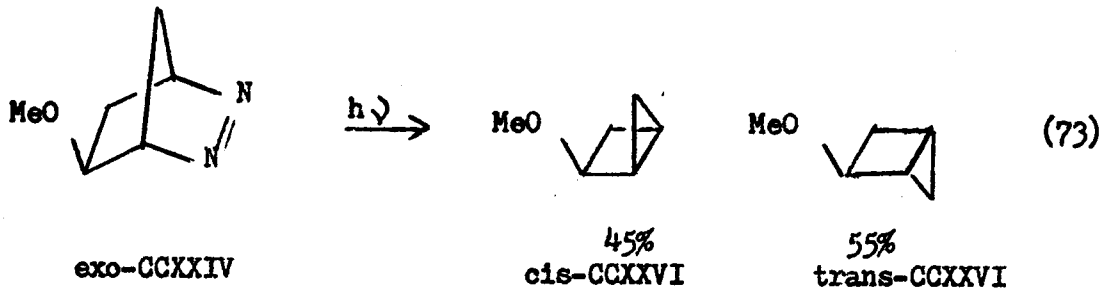
Allred and Smith[80] have studied the thermal decomposition of the endo- and exo-5-methoxy-2,3-diazabicyclo [2.2.1] 2-heptenes, endo-CCXXIV and exo-CCXXIV, respectively. In both cases the major product is the cis isomer, cis- CCXXVI, (93.6% and 63% respectively). The fact that the endo and exo compounds have appreciably different cis/trans product ratios would rule out the possibility of the decomposition's proceeding entirely through a planar intermediate common to both

isomers. Compound endo-CCXXIV proceeds with inversion while Compound exo-CCXXIV proceeds with retention. This result cannot be explained by a single one-step concerted process and it seems unlikely that two compounds of such similar structure would decompose by two different concerted mechanisms. Allred and Smith have proposed the mechanism described in Equation 72 to explain their results. The initial azo compound loses nitrogen in a concerted fashion with inversion of configuration. The inversion is a consequence of the recoil energy released by carbon-nitrogen bond cleavage. The radicals then equilibrate and close. Note that ring closure may precede equilibration of the radicals. It must be noted that the concept of "recoil energy" is somewhat difficult to justify since the reaction of either azo compound to radical is thermoneutral.[81]



(72)

The photochemical behavior of Compounds endo-CCXXIV and exo-CCXXIV provides additional interesting information about this system[80] as shown in Equations 73 and 74. Obviously both reactions proceed with predominant inversion of configuration. Further neither reaction is quenched by piperylene indicating that the reaction intermediate is either a singlet or unquenchable triplet. Benzophenone did sensitize the reaction with the results illustrated in Equations 75 and 76. Clearly there must be a common triplet intermediate involved in these reactions. Also there is no obvious mechanism to explain either the unsensitized or sensitized reaction.

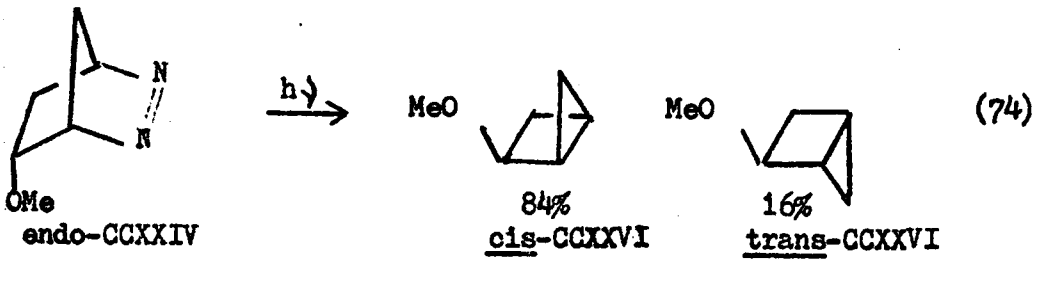


(73)

exo-CCXXIV

45%
cis-CCXXVI

55%
trans-CCXXVI

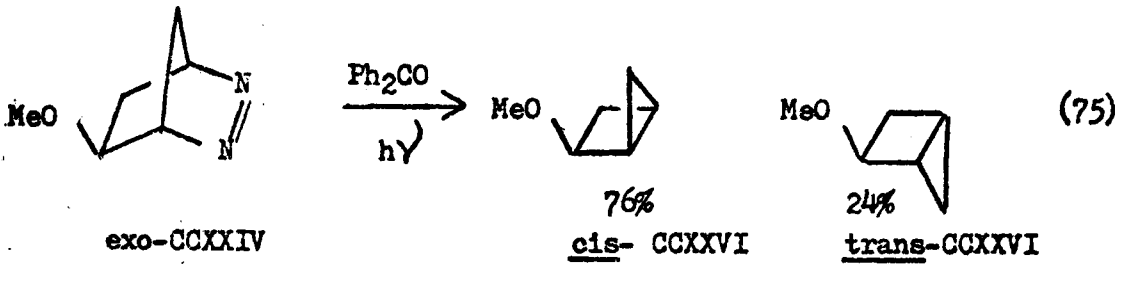


(74)

endo-CCXXIV

84%
cis-CCXXVI

16%
trans-CCXXVI

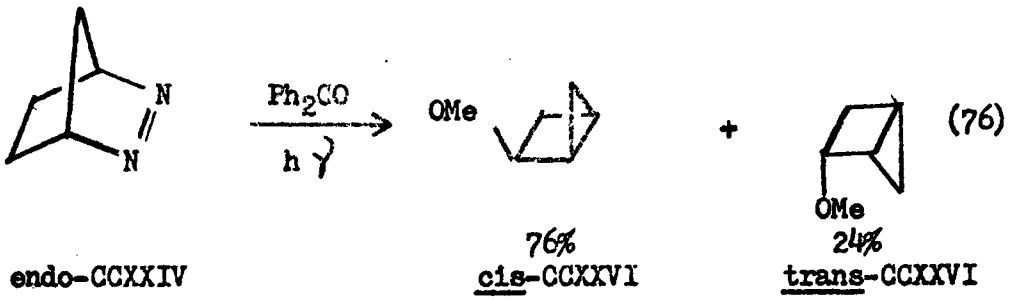


(75)

exo-CCXXIV

76%
cis- CCXXVI

24%
trans-CCXXVI

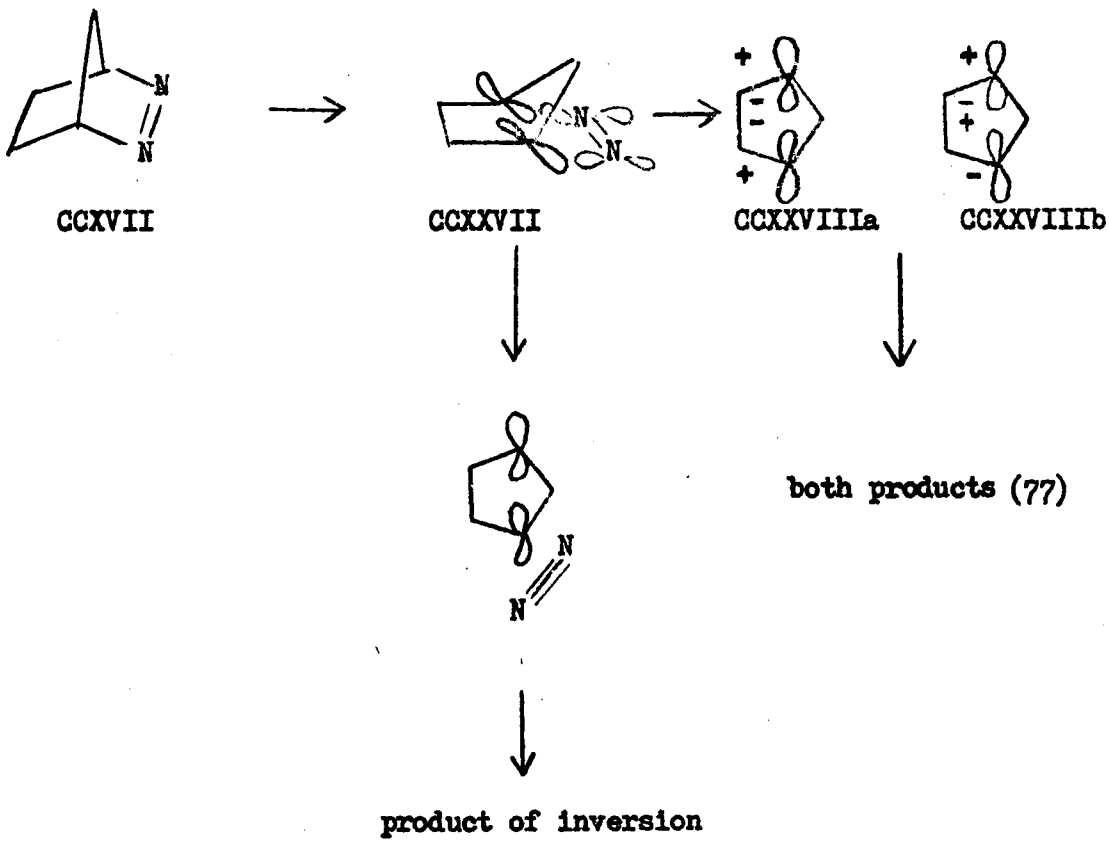


endo-CCXXIV

76%
cis-CCXXVI

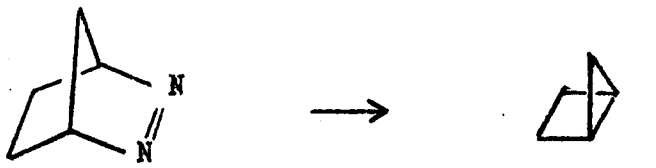
24%
trans-CCXXVI

Trindle and co-workers[82] have considered this reaction from a theoretical point of view. Their basic contention is that the nitrogen molecule is lost as an initial step, yet still asserts considerable influence over the course of reaction although not bonded to the intermediate. Their mechanistic proposal is illustrated in Equation 77.



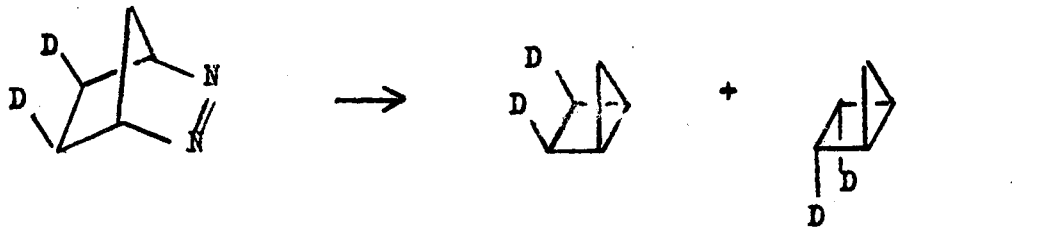
CCXVII CCXXVII CCXXVIIIa CCXXVIIIb

Cohen, Zand and Steel have studied the gas phase decomposition of 2,3-diazabicyclo [2.2.1] -2-heptene.[83] In order to determine the stereochemical mode of the reaction, the dideuterio derivative CCXVIId$_2$ was prepared by Roth and Martin. The products obtained were as shown in Equation 79.[84] The authors favor an explanation of the results by the step-wise elimination shown in Equation 80.



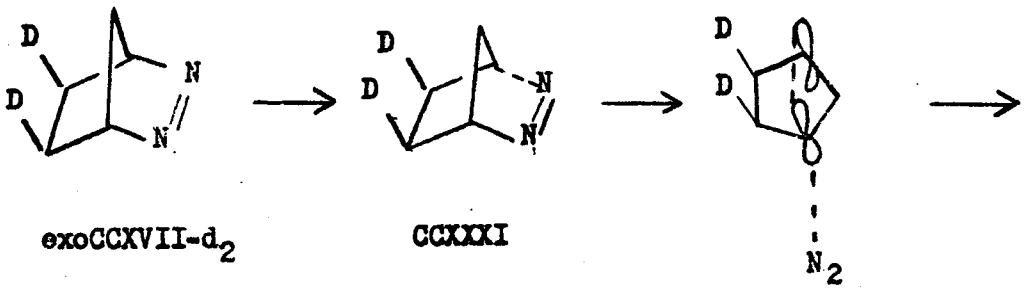
(78)

CCXVII CCCXXX



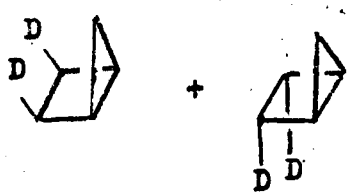
(79)

exo-CCXVII-d$_2$ cis-CCXXX-d$_2$ trans-CCXXX-d$_2$



(80)

exoCCXVII-d$_2$ CCXXXI CCXXIX



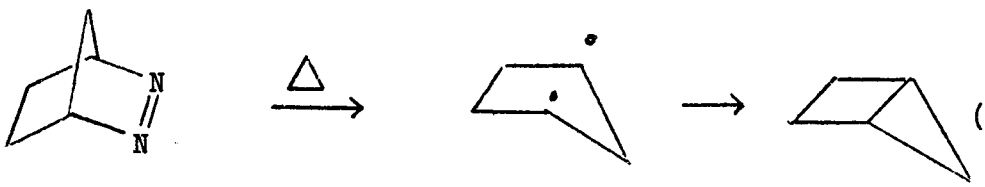
cis- CCXXX-d$_2$ trans-CCXXX-d$_2$

Certainly other mechanisms previously explained should also be considered. Some alternate mechanisms have been described for endo- and exo-5-methoxy-2,3-diazabicyclo [2.2.1] hept-2-ene, endo-CCXXIV (p 79) and exo-CCXXIV (p 79), respectively, and should be equally applicable here.

3. Cyclic Azo Compounds as a Synthetic Tool

As shown in the preceding section the thermal and photochemical decomposition of cyclic azo compounds can occur via either radical intermediates or concerted processes. The diradical can then undergo internal coupling which results in bond formation. Thus both of these routes offer the possibility of a synthetic route to highly strained ring systems.

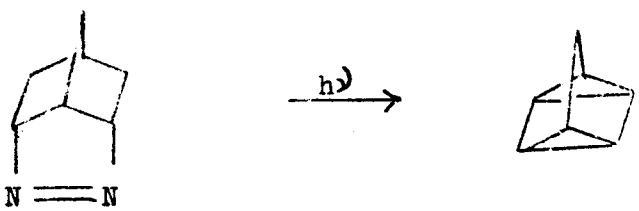
For example, the best synthetic route to bicyclo [2.1.0]-pentane, CCXXX, is the thermolysis of 2,3-diazabicyclo [2.2.1]-hept-2-ene.[85]



(81)

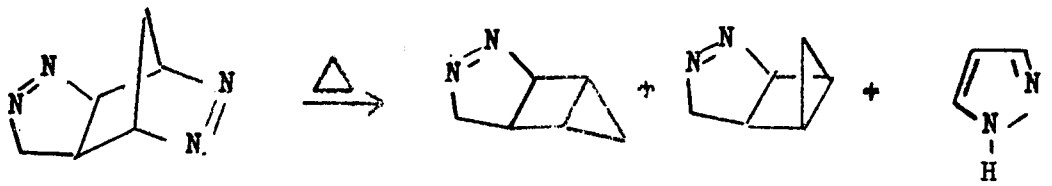
CCXVII CCXXXII CCXXX

Listed below are some further examples of interesting hydrocarbon systems prepared by the decomposition of azo systems.[86]



(82)

CCXXXIII CCXXXIV



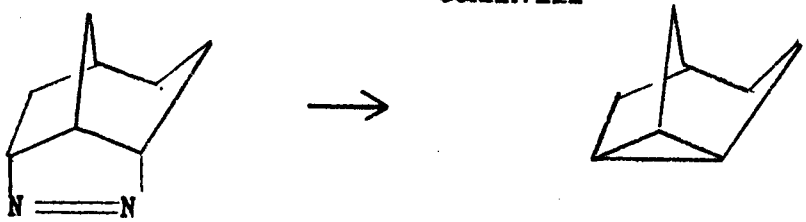
CCXXXV trans-CCXXXVI cis-CCXXXVI CCXXXVII



(83)

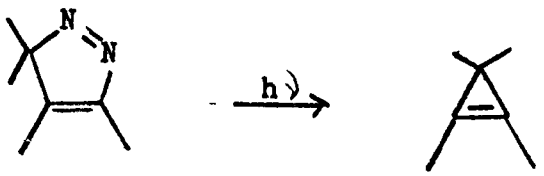


CCXXXVIII



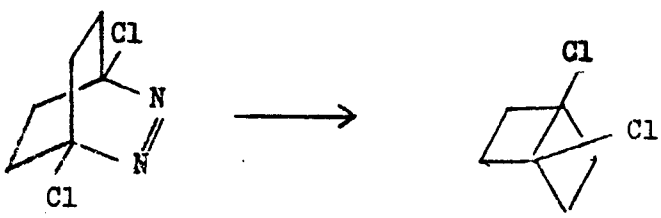
CCXXXIX CCXL

(84)



CCXLI CCXLII

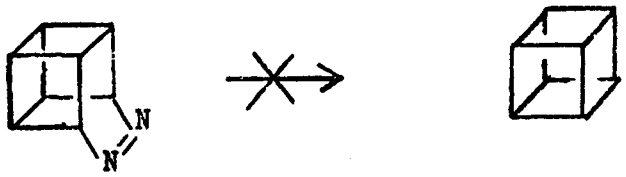
(85)



CCXLIII CCXLIV

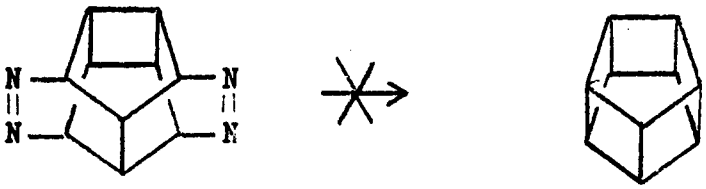
(86)

For reasons not well understood, certain cage azo compounds do not give the expected products of intramolecular bond formation on pyrolysis or photolysis.[86]



(87)

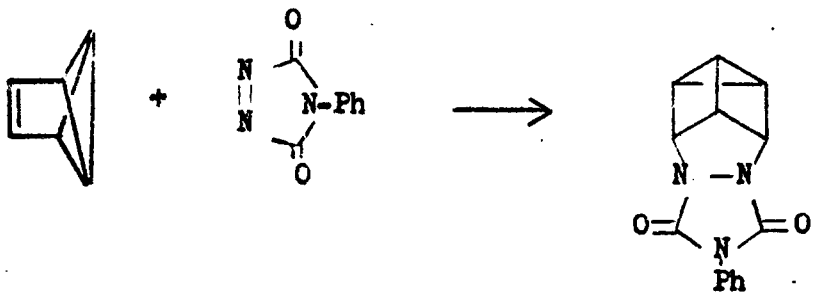
CCXLV CCXLVI



(88)

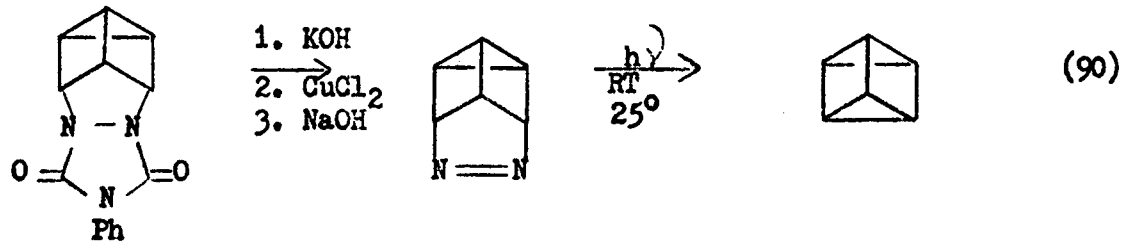
CCXLVII CCXLVIII

Initial reports indicated that prismane or Ladenburg benzene also could not be formed by azo decomposition.[87] However, in 1973 Katz and Acton were able to carry out a most intriguing synthesis of prismane via a cyclic azo intermediate. The reaction sequence is shown below. Earlier attempts at this synthesis apparently failed because the photolysis was carried out at too low a temperature.[88]



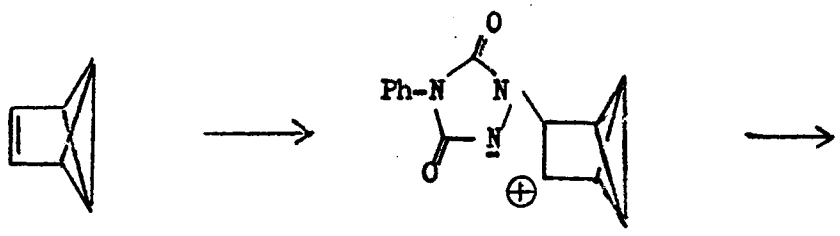
(89)

CCXLIX CLIII

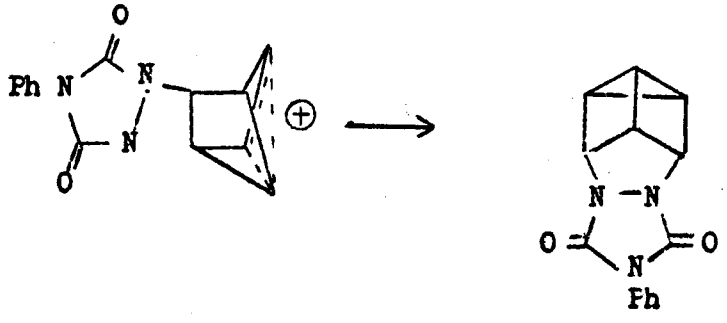


CCL CCLI CCLII (90)

Certainly the reaction leading to Compound CCL is unorthodox and a plausible mechanism has been proposed as shown in Equation 91.

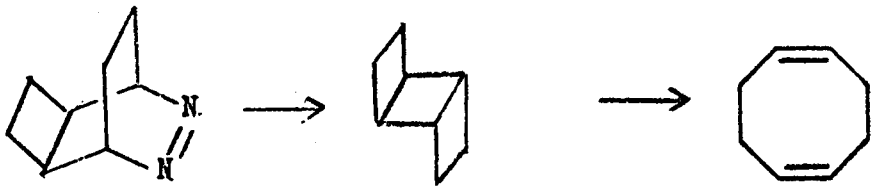


CCXLIX CCLIII (91)



CCLIV CCL

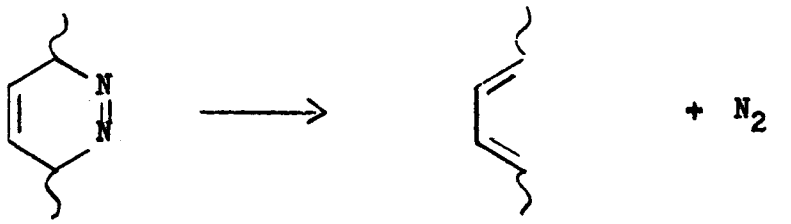
Allred, Hinshaw and Johnson have prepared 1,5-cyclooctadiene via the synthesis shown in Equation 92.[79]



(92)

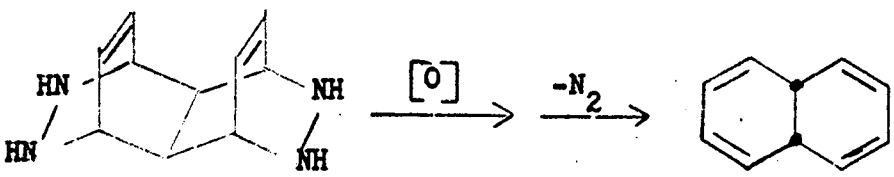
CCXII CCLV CCLVI

In addition to cage compounds a number of sensitive olefins can be obtained under very mild condition by the retro Diels-Alder decomposition of cyclic azo compounds of the general structure as shown in Equation 93. Equations 94 and 95 illustrate this procedure.[86]



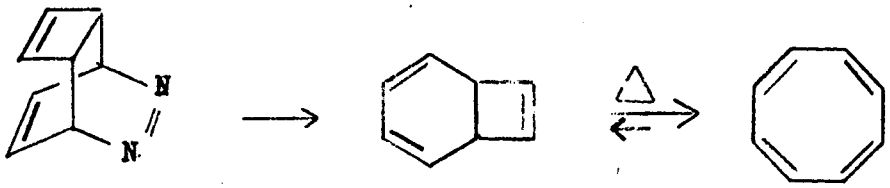
(93)

CCLVII CCLVIII



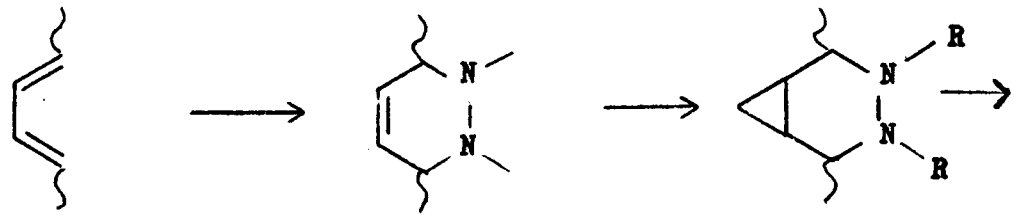
(94)

CCLIX CCCLX

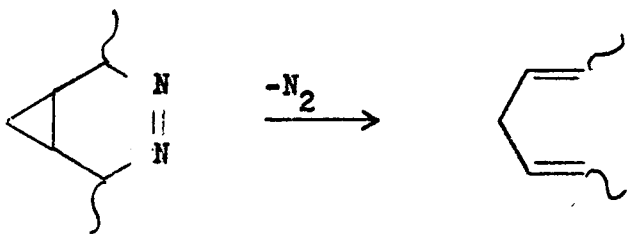


CCLXI CCLXII XIX (95)

A novel route to convert 1,3-dienes to 1,4-dienes is outlined below. The last step is a concerted [2+2+2] cycloreversion.[86]

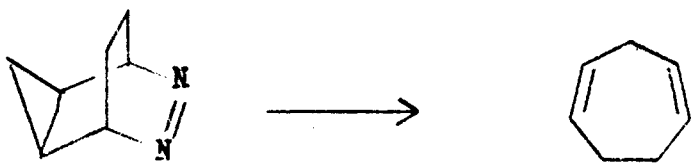


CCLVIII CCLXIII CCLXIV (96)

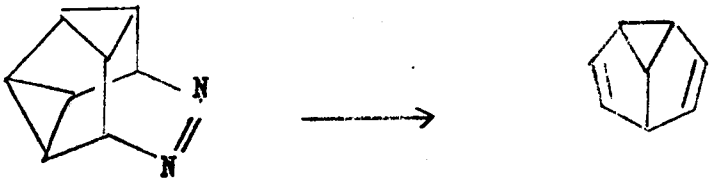


CCLXV CCLXVI

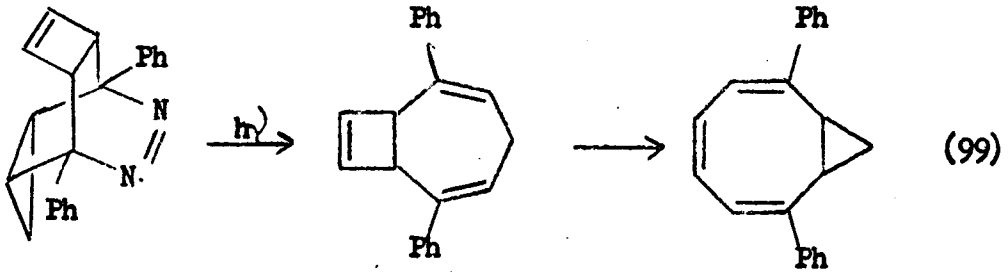
Using the above sequence, polycyclic azo systems can be used to obtain cyclic and polycyclic unsaturated compounds.[70,79]



CCX CCLXVII (97)



CCLXVIII CCLXIX (98)



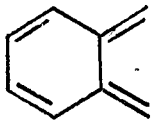
(99)

E. Quinodimethanes

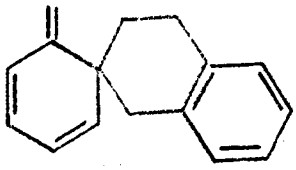
The various benzo- and naphthoquinodimethanes have been the subject of a great deal of theoretical and chemical interest. Huckel theory predicts m-xylylene, 1,3-, 1,6- , 1,8- and 2,7-naphthoquinodimethanes to have triplet ground states. The chemical challenge provided by this class of molecules is described below.

o-Xylylene, CCLXXIII, has been inferred as an intermediate in a number of reactions on the basis of trapping or self-trapping products. The self-trapping products are CCLXXIV, CCLXXV, CCLXXVI and o-xylene. Examples of reactions proceeding via CCLXXIII are oxidation of CCLXXVII (at 0°), thermolysis of CCLXXVIII and CCLXXIX

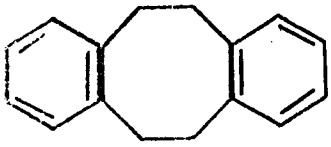
and photolysis of CCLXXX.[89]



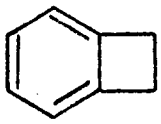
CCLXXIII



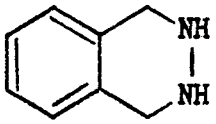
CCLXXIV



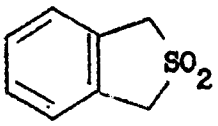
CCLXXV



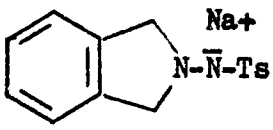
CCLXXVI



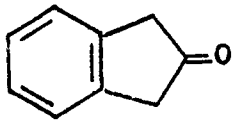
CCLXXVII



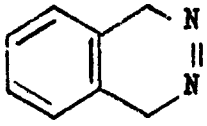
CCLXXVIII



CCLXXIX



CCLXXX

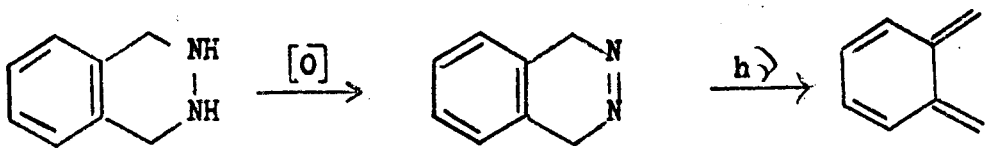


CCLXXXI

Michl and Flynn have recently reported the synthesis of o-xylylene, CCLXXIII, via a matrix isolation technique.[89] The azo precursor, CCLXXXI is prepared by the oxidation of a basic methanolic solution of CCLXXVII at ca. -90° with t-BuOCl. Compound CCLXXXI was then irradiated (2540Å at -196°) producing CCLXXIII which on additional irradiation gave a self-trapping product whose structure was shown to be Compound CCLXXVI.

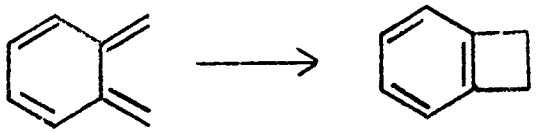
Melting CCLXXIII, the photoproduct of CCLXXXI resulted in the formation of CCLXXIV (another product of self-trapping). As

further proof that the photoproduct of CCLXXXI was indeed CCLXXIII, irradiation at -196° of Compounds CCLXXV, CCLXXVIII, CCLXXIX and CCLXXX gave a photoproduct with identical spectral characteristics to that obtained from irradiation of CCLXXXI as described previously.



(100)

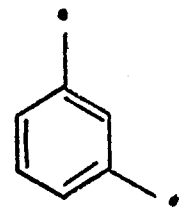
CCLXXVII CCLXXXI CCLXXIII



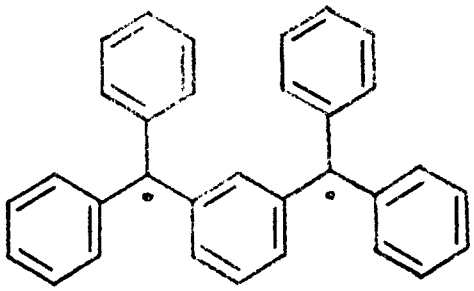
(101)

CCLXXIII CCLXXVI

As stated earlier, m-xylylene, CCLXXXII, is predicted to have a triplet ground state by Huckel theory. As yet it has not been observed directly; however, Luckhurst, et al.,[1] and Kothe Deukel and Summermann[90] have studied the esr behavior of Schlenk's hydrocarbon, CCLXXXIII, and found it to have a triplet ground state.

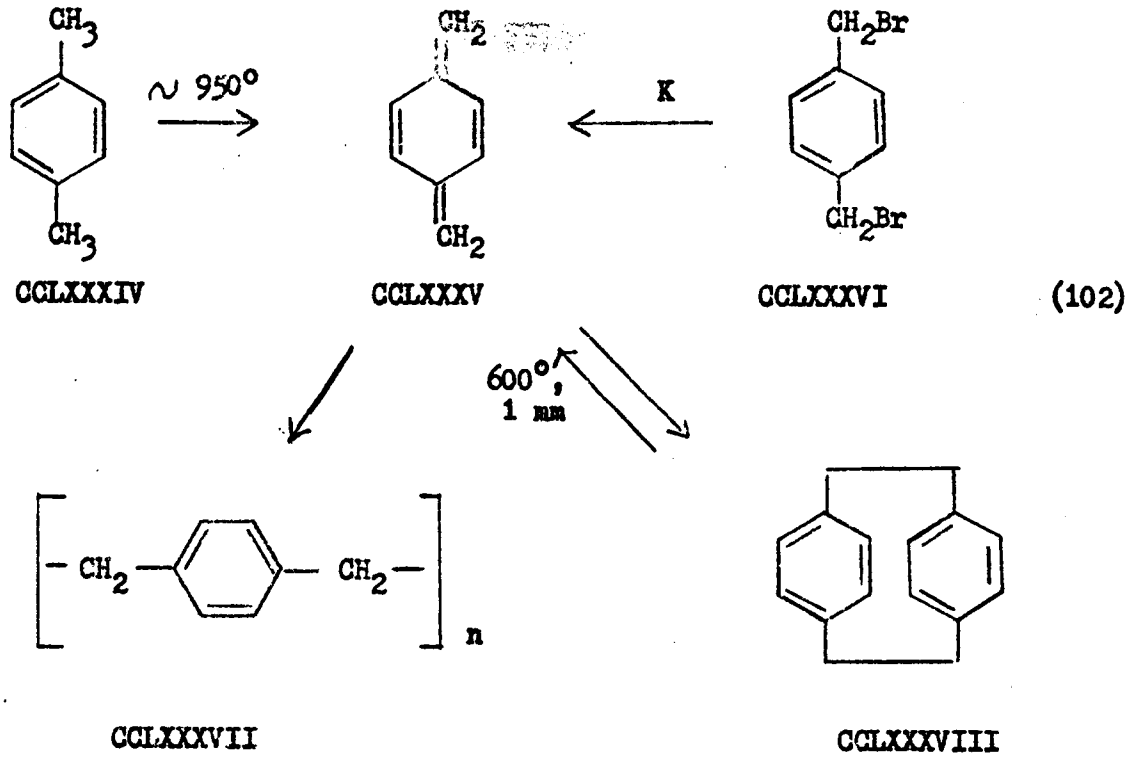


CCLXXXII



CCLXXXIII

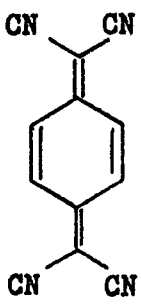
p-Xylylene, CCLXXXV, has been prepared; however, it is highly unstable and is directly observable only at low temperatures in dilute solution.[90] Equation 102 illustrates the various routes to p-xylylene and its products.



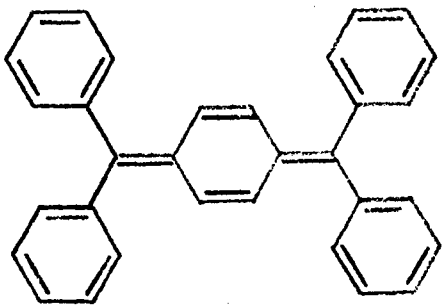
CCLXXXIV CCLXXXV CCLXXXVI (102)

CCLXXXVII CCLXXXVIII

Several interesting compounds containing the p-xylylene structure have been prepared; among them are 7,7,8,8-tetracyanoquinodimethane (TCNQ), CCLXXXIX, and CCXC (a ground state triplet). The 1:1 charge-transfer complex formed by the reaction of TCNQ with tetrathiafulvalene is an organic "superconductor."

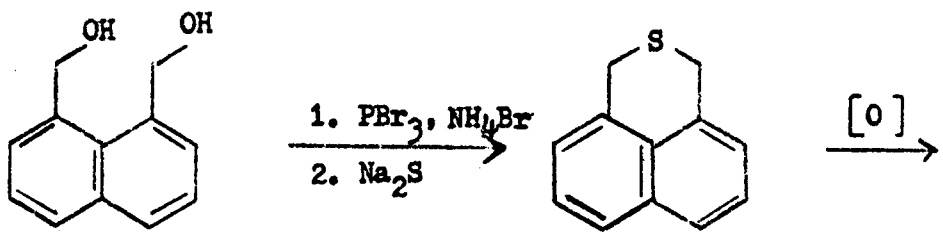


CCLXXXIX

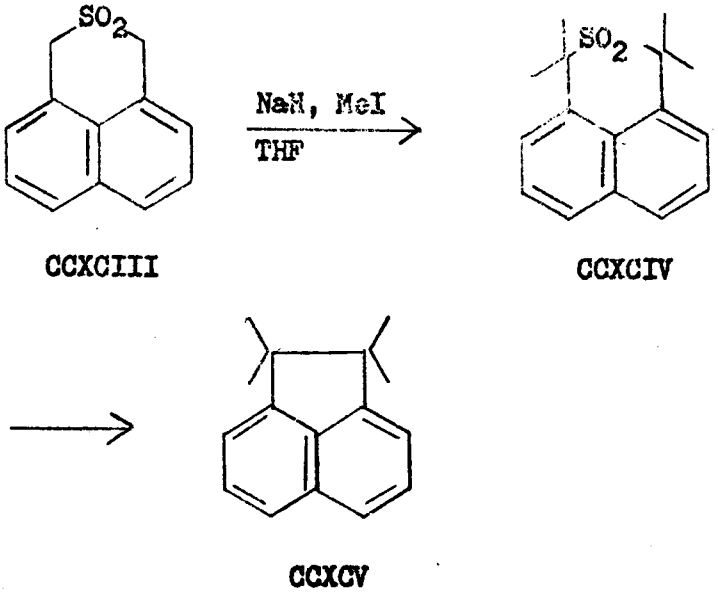


CCXC

Hunter and Stothers[92] used the route shown in Equation 103 to prepare 1,1,2,2-tetramethylacenaphthene, CCXCV. The pyrolysis of Compound CCXCIV to give CCXCV could conceivably go through a 1,8-naphthoquinodimethane intermediate; however, since the temperature required to effect this conversion was significantly higher than that required for compounds yielding orthoquinoidal methanes the authors favored a step-wise decomposition rather than a concerted process.



CCXCI CCXCII

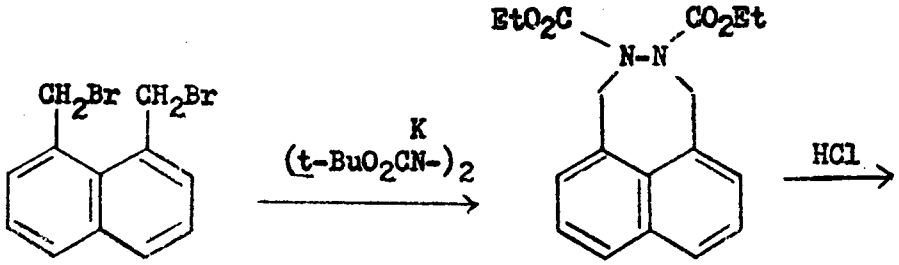


(103)

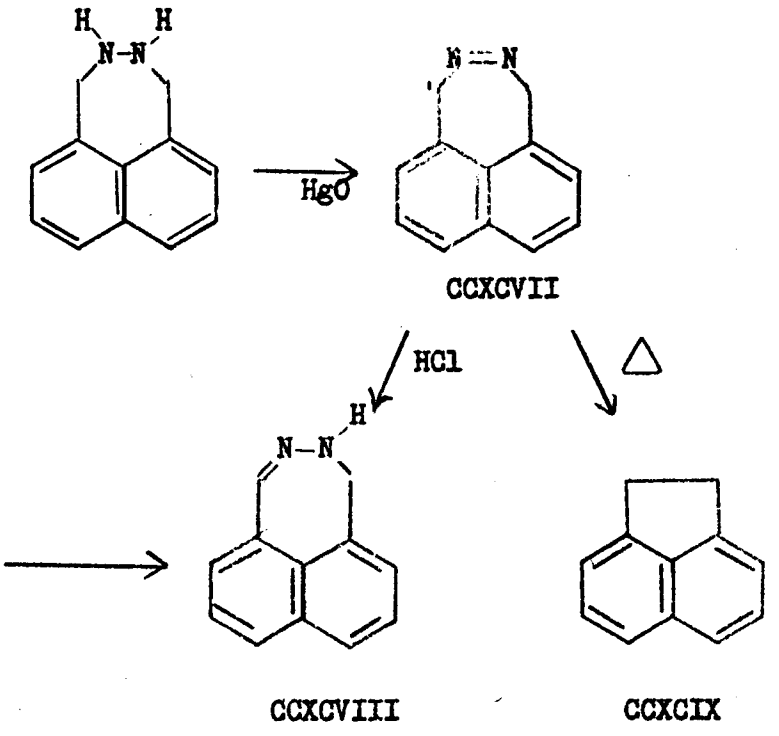
CCXCIII CCXCIV

CCXCV

Carpino has synthesized 1,4-dihydronaphtho [1,8-d,e] [1,2] diazepine, CCXCVII, as shown in Equation 104. Compound CCXCVII was found to rearrange to CCXCVIII on treatment with HCl.[93] On heating, Compound CCXCVII, was found to give acenaphthene, CCXCIX, as its only characterized product.



CCXCVI

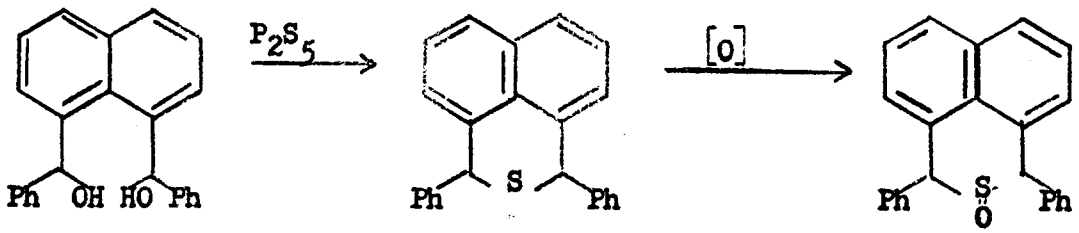


(104)

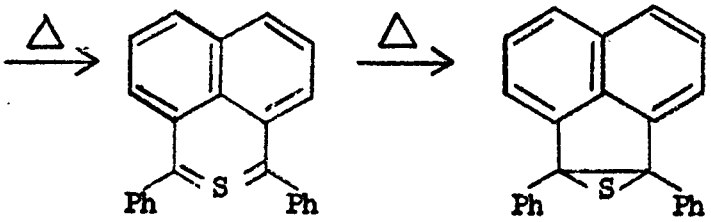
CCXCVII

CCXCVIII CCXCIX

Schlessinger and Schultz[94] were able to prepare a diphenyl substituted derivative, CCCII, by the sequence outlined in Equation 105. Heating CCCII at 120° in degassed acetic anhydride gave CCCV quantitatively. However, heating CCCII at 100° gave a mixture of CCCV and CCCIV. Prolonged heating of CCCIV gave CCCV. Furthermore, thermolysis of CCCII in the presence of N-phenylmaleimide gave the adduct CCCVI. The trapped adduct and product indicate that CCCVII is not an intermediate in this series. This fact in combination with the other data clearly indicates that a 1,8-naphthoquinodimethane is not involved as an intermediate in the pyrolysis of CCCII contrary to expectations. Equation 105 summarizes the results.



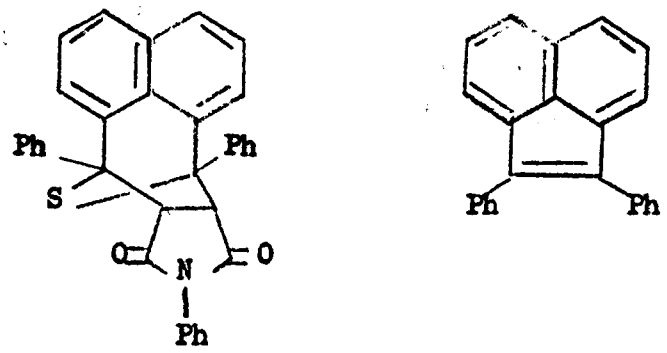
CCC CCCI CCCII



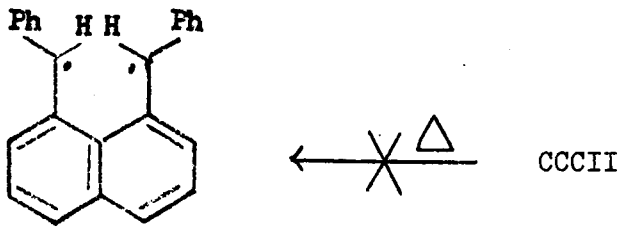
CCCIII CCCIV



(105)



CCCVI CCCV



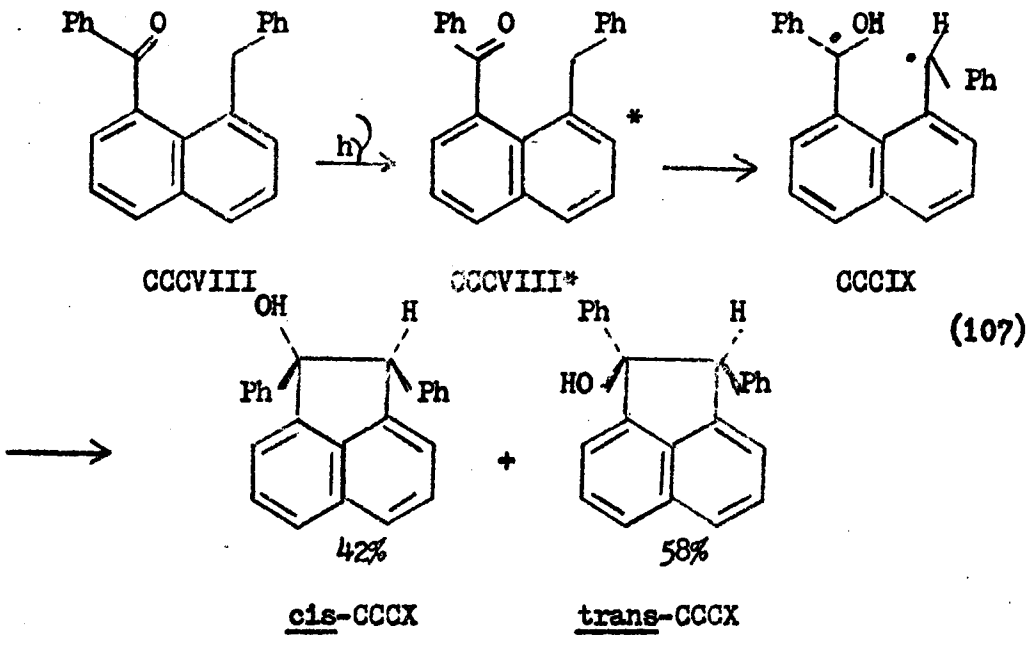
CCCII

(106)

CCCVII

A 1,8-naphthoquinodimethane could be an intermediate in the photochemistry and thermochemistry of 1,8-divinylnaphthalene, 1,8-distyrylnaphthalene and related compounds as reported by Nelsen and Gillespie[95] and by Meinwald and Young.[96] Details of this work will be presented in the next chapter where their discussion is appropriate.

DeBoer and co-workers have prepared and studied the photochemical behavior of 1-benzoyl-8-benzylnaphthalene, CCCVIII. Equation 107 summarizes the photochemical behavior.[97]



CCCVIII → CCCVIII* → CCCIX → cis-CCCX + trans-CCCX (107)

Note that the excited state CCCVIII* is represented as a π,π^* species as opposed to the more commonly encountered n,π^* species for ketones in general. That CCCVIII* is a $^3(\pi,\pi^*)$ was demonstrated by a combination of absorption, phosphorescence, and phosphorescence excitation spectroscopy. The absorption

spectrum showed a weak $^1(n,\pi^*)$ at 405 nm and a much stronger one starting at 325 nm which is quite similar in position and intensity to the first transition of substituted naphthalenes.

The phosphorescence spectrum allowed the states to be ordered. The energy separation between the $^3(\pi,\pi^*)$ and the $^3(n,\pi^*)$ was found to be 8.9 kcal/mole. The approximate phosphorescence lifetime of CCCVIII of 1 sec indicates that the triplet state of CCCVIII is essentially π,π^* with only a small amount of n,π^* character. (Calculations show 8% n,π^* character for CCCVIII).

In the photochemical study of CCCVIII, the excited species CCCVIII* apparently undergoes hydrogen abstraction to yield CCCIX which subsequently undergoes ring closure to form cis- and trans-CCCX in 92% overall isolated yield.

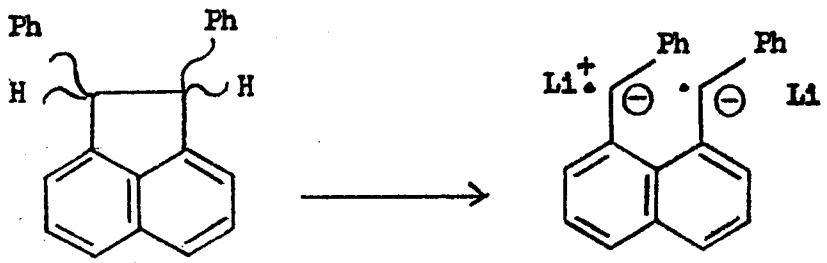
The rearrangement of CCCVIII is completely quenched by the presence of even small amounts of trans-stilbene, oxygen or cyclohexadiene therby, demonstrating that the reaction indeed occurs through the triplet state.

Using flash photolysis techniques it was possible to determine the activation energy for the hydrogen abstraction step at 4.7 kcal/mole. Wagner had previously suggested that the rearrangement of CCCVIII occurred via the thermally excited pure n,π^* state.[97] This cannot be the case since the n,π^* and π,π^* states are separated by 8.9 kcal/mole as stated earlier and the activation energy for the $^3(n,\pi^*)$ to $^3(\pi,\pi^*)$ is typically 5 kcal/mole giving an activation energy of 13.9 kcal/mole for the $^3(\pi,\pi^*)$ to $^3(\pi,n^*)$ transition as opposed to the 4.7 kcal/mole

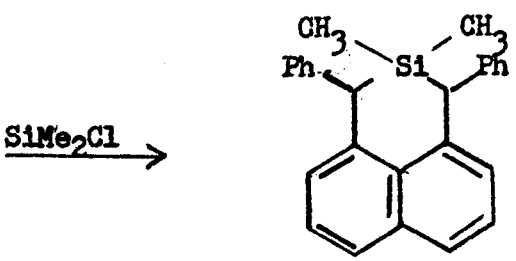
observed. Figure 4 is an energy diagram of the reaction.

Bauld and Hudson[98] recently reported the "first stable-derivative of the 1,8-naphthoquinodimethane series;" however, prelimary reports of a synthesis and characterization of a 1,8-naphthoquinodimethane were presented by this laboratory at regional and national ACS meetings in 1972 and 1973, respectively, and subsequently published in April, 1974, prior to Bauld and Hudson.[99]

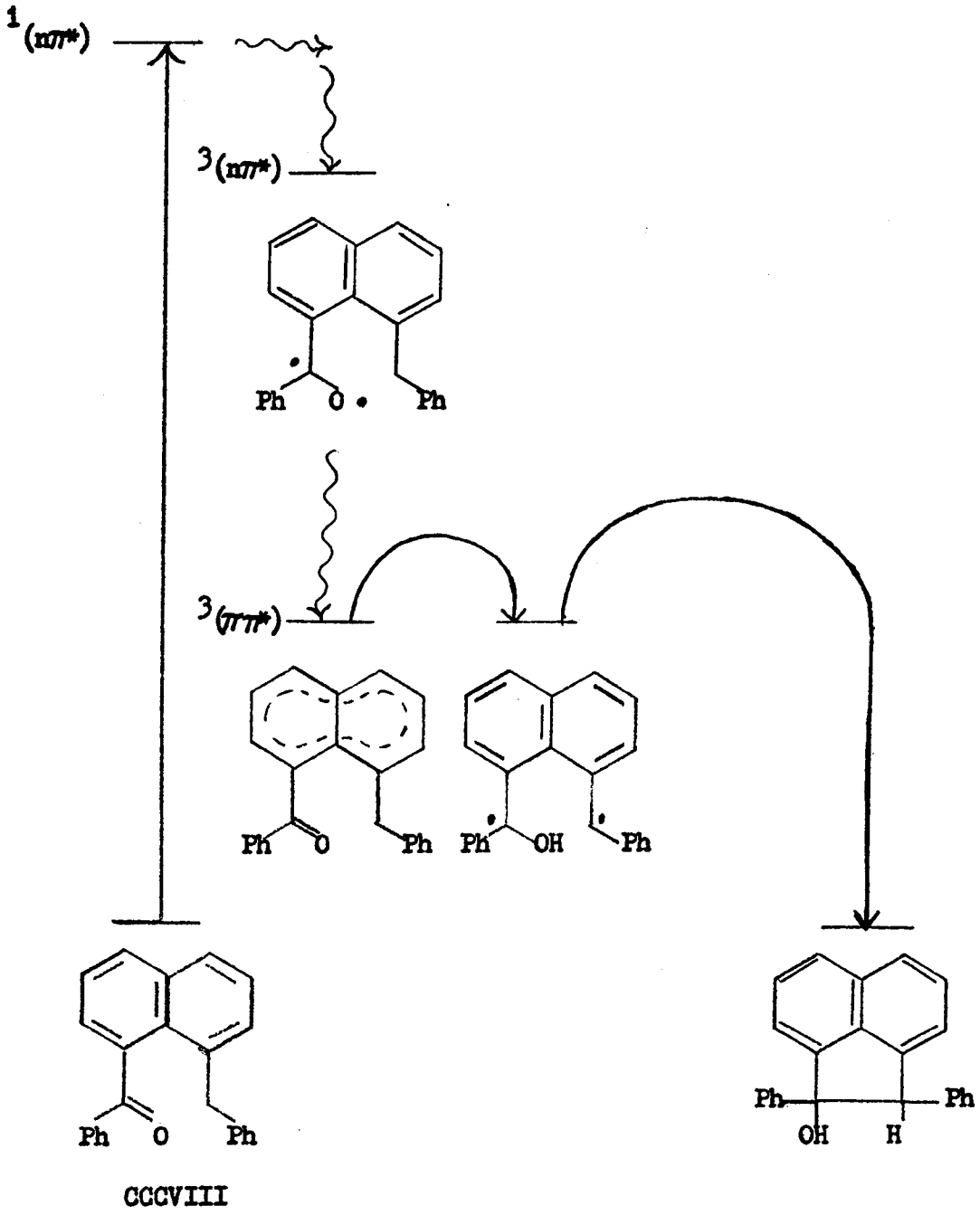
Bauld and Hudson generated the dianion diradical from cis- or trans-CCCX using the lithium salt of the biphenyl radical anion as an electron source since naphthalene has a higher electron affinity than biphenyl. The cleavage of the dianion of CCCX did not occur until the reaction mixture reached 0°C. The dianion resulting from cleavage was trapped using dimethyldichlorosilane giving CCCXII. Nmr subsequently showed Compound CCXII to be the cis isomer.



cis- or trans-CCCX CCCXI (108)



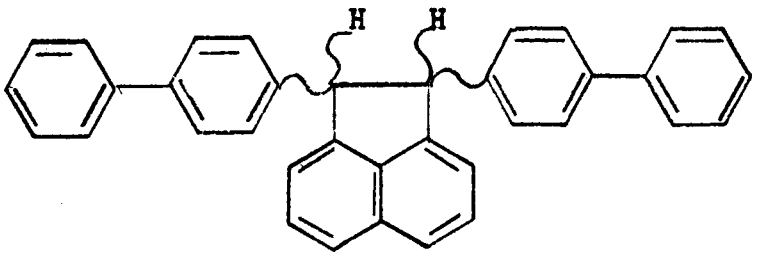
CCCXII



CCCVIII

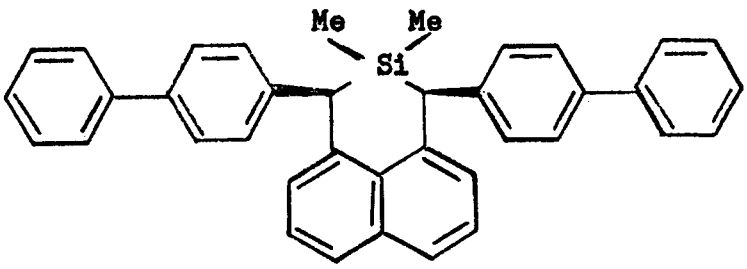
Figure 4. Energy diagram (not to scale) of the rearrangement of CCCVIII.

Cis- and trans-CCCXIII were also prepared in hope that a lower cleavage temperature for the dianion could be obtained due to the conjugating possibilities of the additional para phenyl substituents. Cleavage of cis- and trans-CCCXIII occured in less than 5 minutes at -95°, but quenching still gave the cis-silane from each isomer.



1. $Li^+(Ph)^-$
2. $SiMe_2Cl_2$

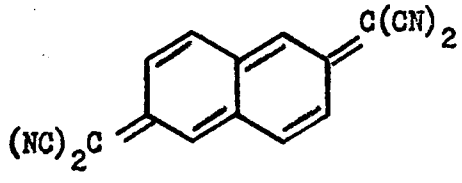
CCCXIII (109)



CCCXIV

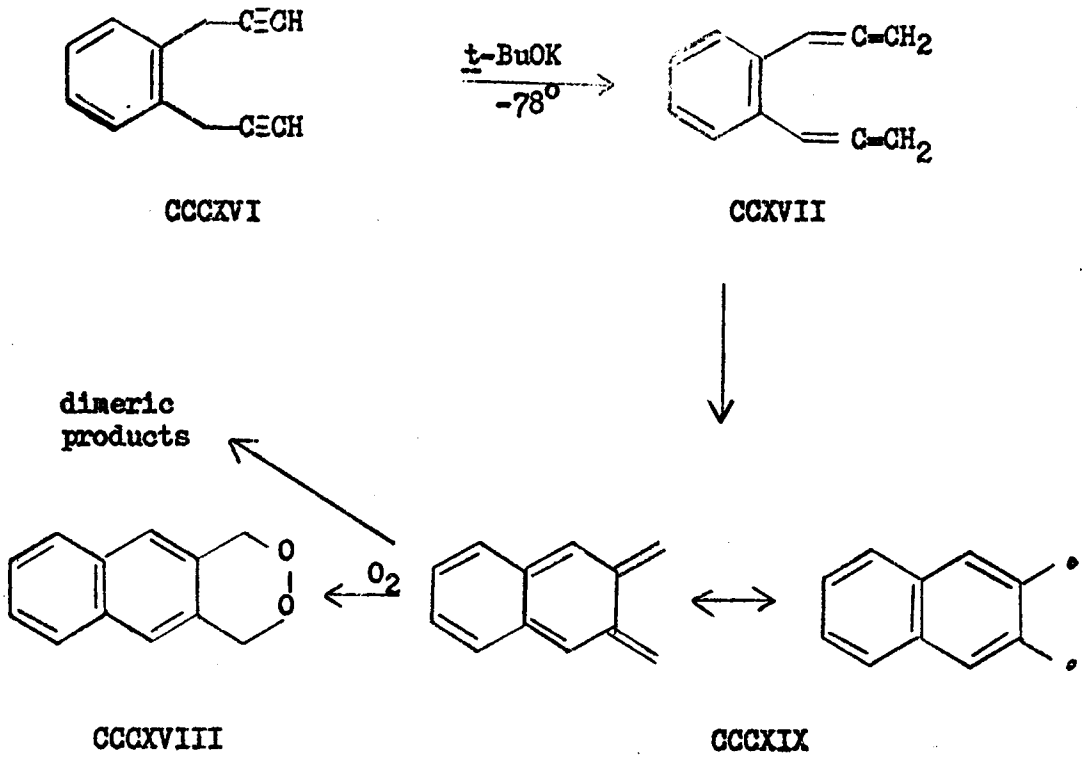
It should be noted that although CCCXI contains the 1,8-naphthoquinodimethane moiety it is in all probability not electronically intact due to the presence of the phenyl substituents.

A stable 2,6-naphthoquinodimethane has been prepared by Garito and others.[91] Its behavior as an electron acceptor in possible superconducting charge-transfer complexes has been studied without success.



CCCXV

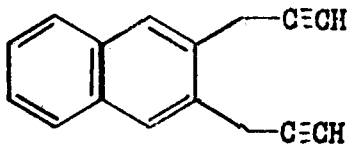
Sondheimer, and co-workers recently undertook a study of the base-catalyzed rearrangement of o-dipropargylbenzene, CCCXVI, in which they observed the products of this reaction to be dimers of 2,3-naphthoquinodimethane, CCCXIX, and the peroxide, CCCXVIII.[100] Compound CCCXVI rearranges to the diallene (CCCXVII) which is then postulated to give rise to CCCXIX which can then either dimerize by a [4+2] cycloaddition or be oxidized to CCCXVIII by triplet oxygen.



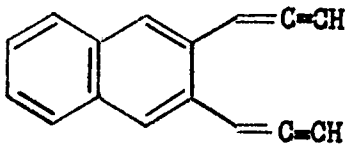
CCCXVI CCXVII

CCCXVIII CCCXIX

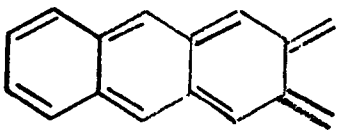
In the same study Sondheimer and co-workers[100] carried out similar reactions with 2,3-dipropargylnaphthalene, CCCXX, and were able to isolate the diallene, CCCXXI, as a crystalline solid. Treatment of this diallene with oxygen-saturated methanol gave the crystalline peroxide (CCCXXI). Again the o-quinodimethane is presumed to be an intermediate as evidenced by the trapping of CCCXXIII with dimethyl fumarate or maleate.

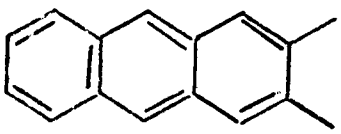


CCCXX



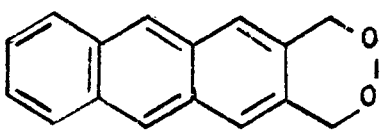
CCCXXI





(111)

CCCXXIII



CCCXXII

CHAPTER II

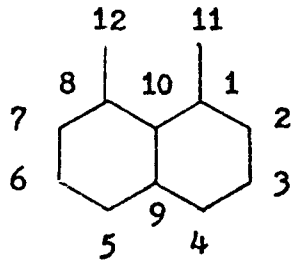
RESULTS AND DISCUSSION

A. Introductory Remarks

As stated in Chapter I, Huckel theory predicts that the ground state of 1,8-napthoquinodimethane, XVII (p 12), should be a triplet.[101] Table III illustrates the ordering of the energies of the Huckel molecular orbitals for this twelve π electron system. In the ground state of this molecule, ten of the electrons are contained in five bonding MO's, each of which contains two paired electrons. The remaining two π electrons are then placed in the next highest available energy level which consists of two degenerate nonbonding MO's located at E = 0 in this case. One of these nonbonding MO's is symmetric (S) with respect to a plane bisecting the molecule through the C_9 - C_{10} bond, while the remaining MO is antisymmetric (A) to this plane. Since the two MO's are degenerate, Hund's rule requires that one of the electrons go into the S MO while the other electron must be placed in the A MO with the spins unpaired. The net result of this order of electron filling is that the ground state of XVII (p 12) is predicted to be a triplet. Since the degenerate molecular orbitals of XVII (p 12) at E = 0 are not related by some element of symmetry, the molecule may be further described as a heterosymmetric triplet under the definition of Salem and Rowland (p 12).[4]

TABLE III

SUMMARY OF HUCKEL CALCULATIONS FOR 1,8-NAPHTHOQUINODIMETHANE[101]

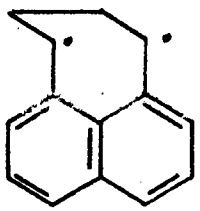


	COEFFICIENTS						
Position	1	2	3	4	5	6	7
Energy	2.39417	1.73205	1.50597	1.00000	1.00000	0.00000	-0.00000
Symmetry	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
1	0.35355	0.35355	-0.35355	-0.35355	0.00000	0.00000	0.00000
2	0.23293	0.40825	-0.09922	0.00000	-0.40825	-0.40825	-0.19612
3	0.20412	0.35355	0.20412	0.35355	-0.40825	0.00000	0.00000
4	0.25578	0.20412	0.40663	0.35355	0.00000	0.40825	0.19612
9	0.46586	0.00000	-0.19845	0.00000	0.40825	0.00000	-0.39223
10	0.40825	0.00000	0.40825	0.00000	0.40825	0.00000	0.00000
11	0.14767	0.20412	-0.23477	-0.35355	0.00000	0.40825	0.58835

As noted in Chapter I, a number of chemical systems have been reported in the chemical literature in which a 1,8-naphthoquinodimethane, XVII (p 12), could be an intermediate. However, no example has been presented in which of a 1,8-naphthoquinodimethane has been characterized or proven to exist. The intent of the remaining portion of this dissertation is to describe the first successful characterization of a 1,8-naphthoquinodimethane, XVII (p 12).

Ideally it would be desirable to study a planar 1,8-naphthoquinodimethane, XVII (p 12), directly since the Hückel prediction of a triplet ground state for XVII (p 12) is based on a totally planar structure. Unfortunately, a direct study of planar XVII (p 12) does not appear to be feasible since the traditional approaches to this system have consistently failed to produce definitive results.[93,94,97,98,100] Molecular models strongly sggest that the steric interaction between the hydrogen atoms on the peri-substituents of XVII (p 12) would effectively prevent the molecule from attaining planarity even if it could be prepared. Further, as a result of the close proximity of the peri methylenes, there may be direct electronic interaction or overlap between the nonbonded orbitals on these groups. As a consequence of these steric and electronic interactions, the Huckel prediction of a triplet ground state for XVII (p 12) may be based on an inadequate model. These complications

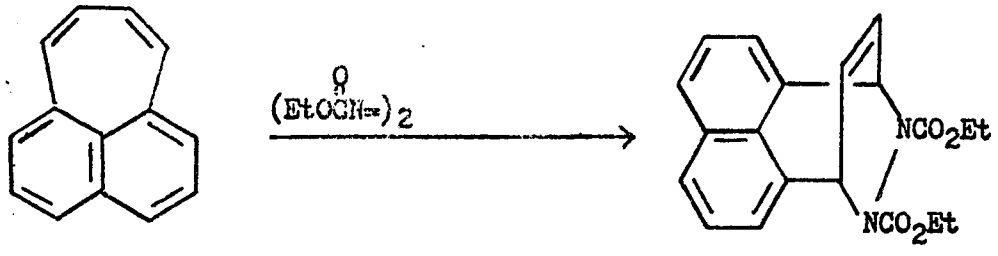
make the nature of the ground state of XVII (p 12) a most intriguing question. For these reasons it was decided to approach the study of XVII (p 12) via the bridged homolog, Compound CCCXXIV. It was hoped that this approach would eliminate a portion of the unfavorable steric interaction as well as provide stereochemical information which would be unavailable even from a successful study of Compound XVII (p 12). In addition the presence of the two carbon bridge greatly facilitates the synthetic accessibility of CCCXXIV as will be demonstrated in the following section. It should be noted that the work of Carpino[93] (p 94) does suggest that a direct study of XVII (p 12) might be feasible.



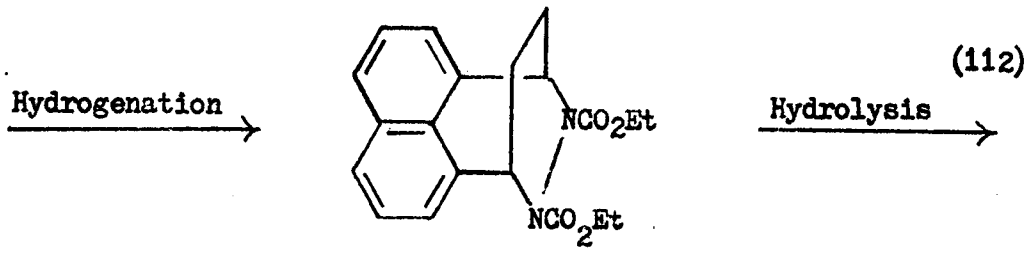
CCCXXIV

B. Synthetic Approach

An obvious and appealing synthetic route to CCCXXIV is through the thermal and/or photochemical decomposition of the azo compound, CCCXXV, as illustrated in Equation 112.[102]

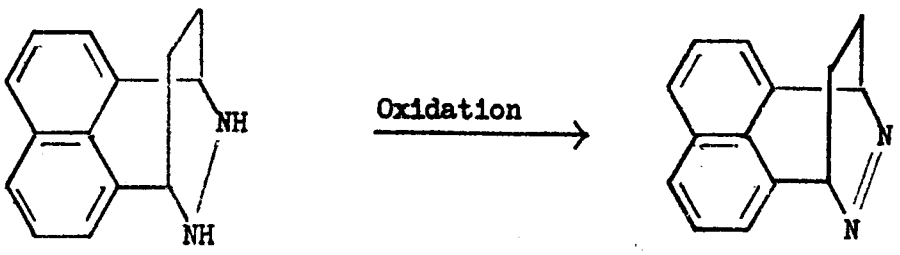


CCCXXVI CCCXXVII



(112)

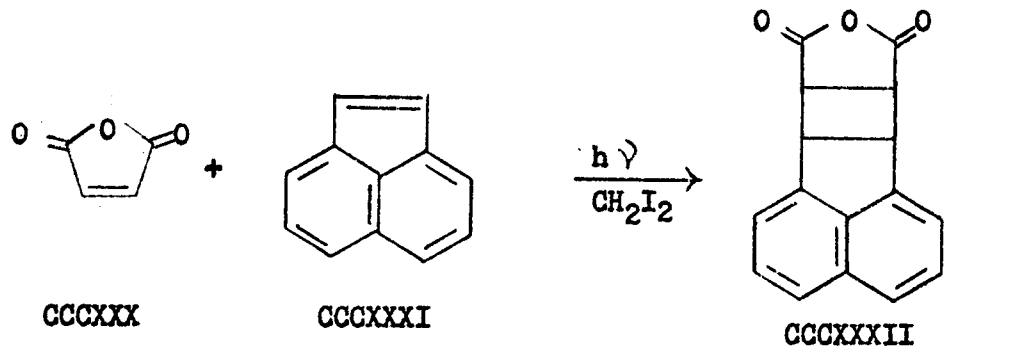
CCCXXVIII



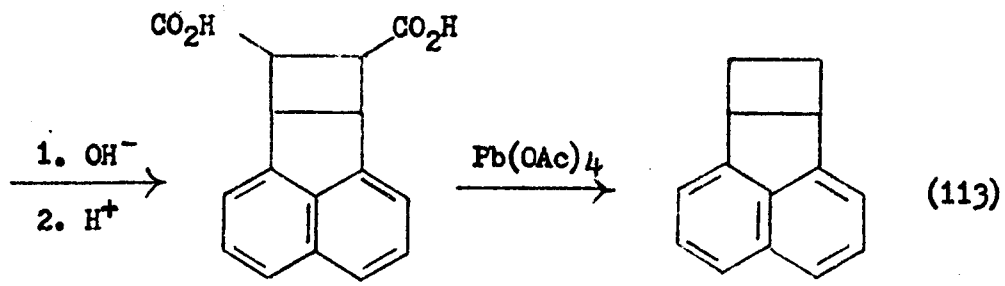
CCCXXIX CCCXXV

Obviously, the success of this synthetic approach hinges on the availability of pleiadiene, Compound CCCXXVI. Various syntheses of pleiadiene have been available for quite some time although none

of them is of very high yield or easily carried out.[103,104] Of the available routes, the best was a sequence developed by Meinwald, et al., as described in Equation 113.[104]

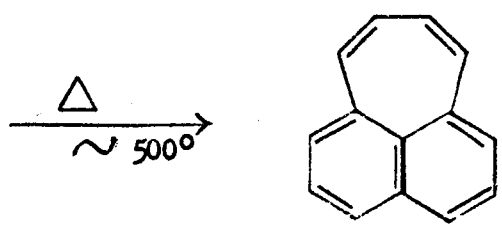


CCCXXX CCCXXXI CCCXXXII



CCCXXXIII CCCXXXIV

(113)



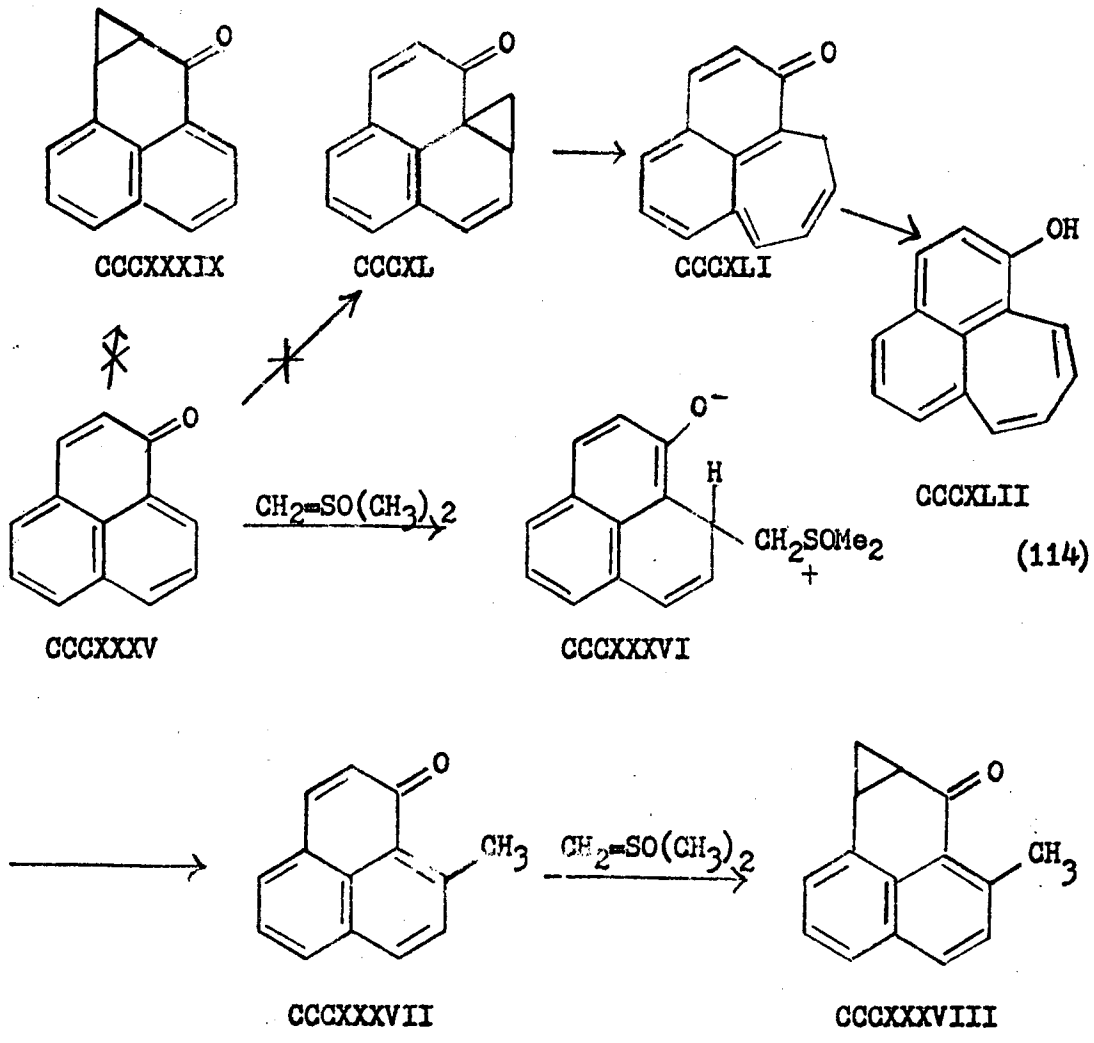
CCCXXVI

In general, attempts at photochemical additions involving acenaphthalene give only dimers; however, when the photolysis is carried out in the presence of methylene iodide, maleic anhydride is found to undergo a [2+2] cycloaddition with acenaphthylene giving Compound CCCXXXII (p 110) in isolable (if not spectacular) yield. Further, the reaction is difficult to scale up to any significant degree due to the physical limitations of available commerical photochemical reactors. As a result only relatively small amounts of Compound CCCXXXII (p 110) could be prepared in a reasonable time period. The hydrolysis of CCCXXXII (p 110) to CCCXXXIII (p 110) provided a convenient solution to the otherwise difficult task of separating the desired product from the unreacted starting materials, dimers and polymer. The oxidation of Compound CCCXXXIII (p 110) to CCCXXXIV (p 110) by lead tetracetate (LTA) was also a low yield reaction. It was found in this laboratory that the yield of CCCXXXIV (p 110) could be increased to approximately 30% when the oxidation was carried out in an oxygen atmosphere. This observation was independently verified by Nelsen and Gillespie in a recent paper.[95] In an effort to improve the yield of this bisdecarboxylation step, a Kolbe electrolysis on CCCXXXIII (p 110) was carried out in pyridine using tin and platinum electrodes. Unfortunately the experiment was an utter failure.

Fortunately, once CCCXXXIV (p 110) had been prepared and isolated it could be converted into pleiadiene, CCCXXVI (p 109), in high yield in one pass through a nitrogen flushed flow pyrolysis

apparatus maintained at $500^{\circ} \pm 10^{\circ}$. This is in contrast to the results of Meinwald and co-workers who found several passes at 400° to be necessary for complete conversion of Compound CCCXXXIV (p 110) into pleiadiene, CCCXXVI (p 109).[104]

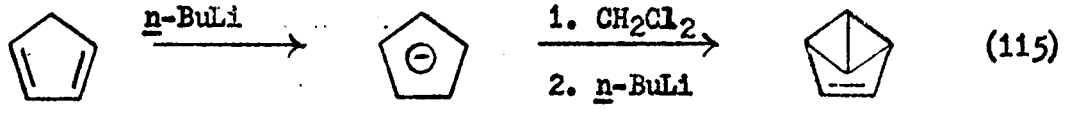
In order to overcome the above synthetic difficulties in the preparation of pleiadiene a number of alternate synthetic procedures were attempted. In one such attempt the reaction of dimethyloxosulfonium methylide with phenalenone, CCCXXXV, was investigated. The anticipated product of this reaction was either 1-hydroxypleiadiene, CCCXLII, or the cyclopropyl Compound CCCXXXIX, which conceivably would be converted into pleiadiene.[106] Unfortunately, when the reaction was carried out, the major product was Compound CCCXXXVII. On further reaction with dimethyloxosulfonium methylide, Compound CCCXXXVII, gave Compound CCCXXXVIII.[106] In the first reaction, C_9 is probably attacked by the dimethyloxosulfonium methylide in preference to C_3 due to complexation of the reactants. In the case of attack on CCCXXXVII, the 9-position is already hindered; hence, attack occurs at C_3. With Compound CCCXXXVI the 1,2-hydride shift probably takes place in order to preserve the aromaticity of the naphthalene nucleus instead of the molecules undergoing the more common cyclopropyl ring closure. Obviously, the preservation of aromaticity is not a problem in the formation of CCCXXXVIII and production of the cyclopropyl ring occurs readily.



(114)

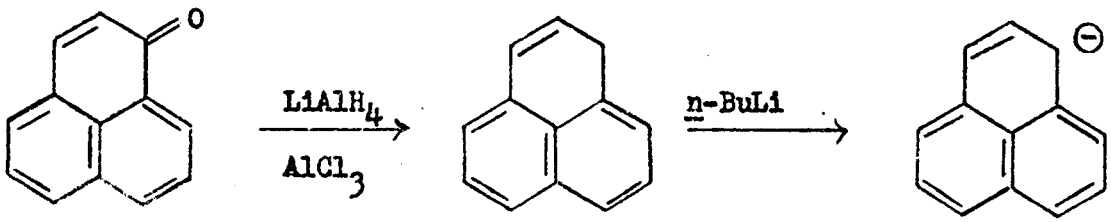
A more successful approach to the synthesis of pleiadiene was suggested by the work of Katz and co-workers who had developed a procedure for the synthesis of benzvalene, Compound CCXLIX (p 85), benzobenzvalene, CCCXLIX, and isobulvalene, CCCL.[107] Their procedurs for the synthesis of benzvalene, CCXLIX (p 85), is illustrated in Equation 115. Using this precedent and having

previously developed a high yield synthesis of phenalene from phenalenone,[105] it was hoped that a satisfactory procedure could worked out for the synthesis of pleiadiene from phenalene. In order to carry this out, an ether solution of phenalene was treated with n-butyl lithium at room temperature. This treatment was followed by methylene chloride and n-butyl lithium at -70° to -75°. Work-up of the reaction mixture afforded a mixture of two products in a ratio of 1 to 4. It was found that these two products could be purified by column chromatography and separated by repeated recrstallization from ligroine. The minor product was identified as pleiadiene, CCCXXVI (p 110), and the major product was found to be Compound CCCXLVIII which was given the trivial name Knoxvalene.[107] These results are summarized below in Equation 116.

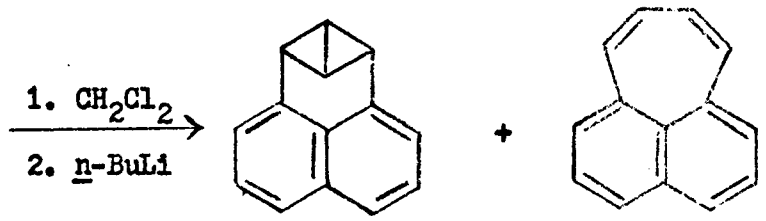


(115)

CCCXLIII CCCXLIV CCCXLV

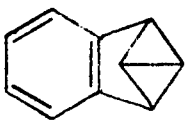


CCCXXXV CCCXLVI CCCXLVII



(116)

CCCXLVIII CCCXXVI





CCCXLIX CCCL

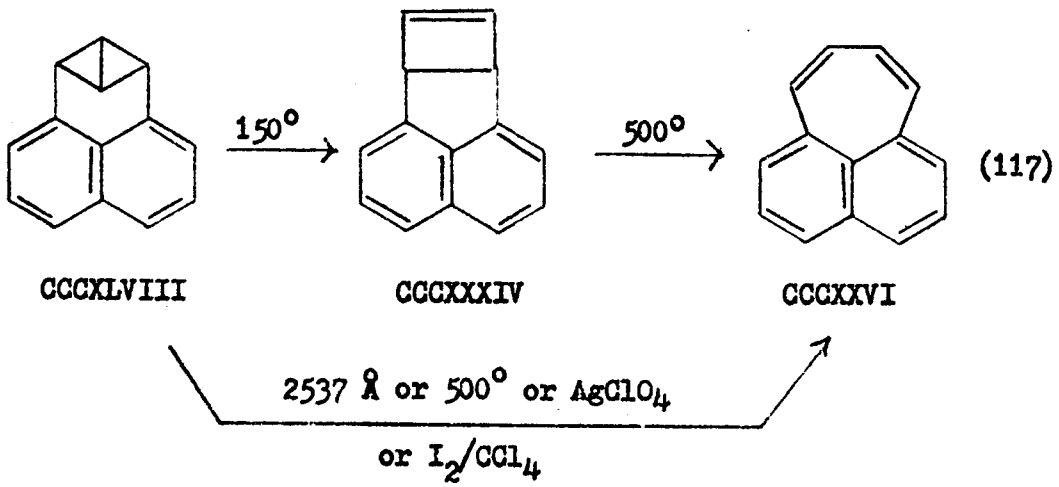
It should be noted that Murata and Nakasuji, who reported the above synthesis of CCCXLVII, and CCCXXVI (p 110) concurrently with this laboratory,[108] have recently extended this synthetic approach to other systems and thereby illustrated its generality.[109]

In order to ascertain the chemical nature of Knoxvalene, CCCXLVIII, it was desirable to develop a facile and efficient procedure for its separation from pleiadiene. It was found that refluxing the product mixture in either benzene or carbon tetrachloride with diethyl azodicarboxylate gave two products. They were identified as the Diels-Alder adduct of pleiadiene, CCCXXVI (p 109), and diethyl azodicarboxylate, Compound CCCXXVII (p 109), and unreacted Knoxvalene, CCCXLVIII. A priori one might have expected Knoxvalene to have reacted with diethyl azodicarboxylate. However,

the reaction would have to be iniatiated from the underside of the bicyclobutyl ring if the back lobes of the orbitals forming the bridging bond are to be attacked as would be anticipated. This approach is effectively blocked by the naphthalene substituent and control experiments showed Knoxvalene, CCCXLVIII (p 115) to be completely inert under the reaction conditions described above.[110] The blockage of the underside of the bicyclobutyl group of Compound CCCXLVIII (p 115) is so effective that Knoxvalene, CCCXLVIII (p 115) did not react with N-phenyltriazolinedione in acetonitrile solution when stirred overnight.[110]

Since the original object in developing the synthesis in which Knoxvalene, CCCXLVIII (p 115), was produced was to obtain a better synthetic route to the isomeric pleiadiene, CCCXXVI (p 109), it was obviously highly desirable to develop a high yield method for the conversion of Knoxvalene, CCCXLVIII (p 115), into pleiadiene, CCCXXVI (p 109). Fortunately a variety of high yield methods were readily developed both in this laboratory and elsewhere.[107,108] Moderate heating (150°) of a sealed tube containing a benzene or cyclohexane solution of Knoxvalene converted it into Compound CCCXXXIV (p 110). Compound CCCXXXIV (p 110) is the direct precursor to pleiadiene, CCCXXVI (p 109), by Meinwald's procedure as seen previously (p 110). As would be expected, pleiadiene could be produced directly from Knoxvalene, CCCXLVIII (p 115), by injecting a hexane solution of the compound into a flow pyrolysis tube at 500°.[107] Since control experiments showed that pleiadiene was

unaffected by as many as three passes through the pyrolysis apparatus, it was unnecessary to separate Knoxvalene, CCCXLVIII (p 115), from pleiadiene, CCCXXVI (p 109), for preparative purposes. Other procedures which have been developed for the conversion of Knoxvalene, CCCXLVIII (p 115), into pleiadiene, CCCXXVI (p 109), include irradiation of Knoxvalene, CCCXLVIII (p 115), at 2537Å,[107] treatment with $AgClO_4$ in benzene [108] and treatment with a catalytic amount of iodine in carbon tetrachloride.[110] The yields of pleiadiene, CCCXXVI (p 109), by these procedures range from 60 to 80% and recent results suggest that the treatment of Knoxvalene, CCCXLVIII (p 115), with iodine is the method of choice for the conversion into pleiadiene since the reaction is essentially instantaneous at room temperature and work-up is obviously quite simple.[110]



(117)

Having established a practical route to pleiadiene, the preparation of the desired bicyclic azo compound, CCCXXV (p 109), was undertaken. As noted previously (p 115), the Diels-Alder adduct, Compound CCCXXVII (p 109), which was obtained as the reaction product of pleiadiene, CCCXXVI (p 109), and diethyl azodicarboxylate in refluxing benzene or carbon tetrachloride. Compound CCCXXVII (p 109) is a glassy solid which can be readily isolated and purified by column chromatography on alumina.

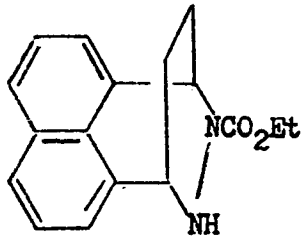
The nmr of Compound CCCXXVII (p 109) is in itself quite interesting since the compound apparently exists in a variety of conformations. In support of this view, the two ethyl groups are non-equivalent as evidenced by the observation of a very complex methyl signal appearing as a multiplet at 0.7 to 1.4δ. The methylenes of these two ethyl groups appear as an equally complex multiplet at 3.6 - 4.4δ. Further, the bridgehead protons are likewise non-equivalent and appear as complex multiplets at 5.4 - 5.7δ and 5.8 - 6.1δ. The vinylic protons appear as a broad multiplet at 6.3 - 6.6δ.

The conversion of Compound CCCXXVII (p 109) into CCCXXVIII (p 109) was achieved by the atmospheric hydrogenation of an ethanol solution of CCCXXVII (p 109) in the presence of Adam's catalyst. In an alternate procedure diimide was used to hydrogenate CCCXXVII (p 109) with satisfactory results.[110]

When Compound CCCXXVII (p 109) was hydrogenated, the vinylic signal at 6.3 - 6.6δ disappeared and a very broad complex multiplet

appeared at 2.1 - 2.6δ representing four protons. The remainder of the spectrum was essentially identical to that of Compound CCCXXVII (p 109) with some minor shifts in the positions of the chemical shifts of the signals which will be enumerated in the experimental portion of this dissertation.

When Compound CCCXXVIII (p 109) was refluxed in alcoholic KOH for eight hours, work-up gave Compound CCCXXV (p 109) directly. It proved to be impossible to isolate CCCXXIX (p 109) although it is almost certainly an intermediate. If the hydrolysis was interrupted before the reaction had reached completion, a product having an nmr spectrum compatible with the half-ester, CCCLI, was obtained. Presumably this half-ester is further hydrolyzed to CCCXXIX (p 109) which then loses hydrogen to give CCCXXV (p 109).



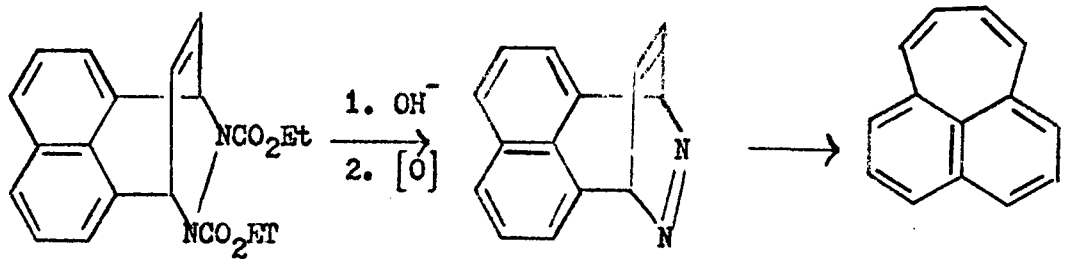
CCCLI

The nmr spectrum of Compound CCCXXV (p 109) was quite simple consisting of an aromatic region at 7.3 - 7.9δ, a broad singlet at 6.0 - 6.2δ representing the two bridgehead protons and a doublet at

2.0 - 2.6δ representing the four methylene protons.

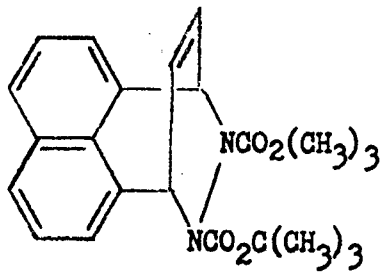
When a sample of CCCXXV (p 109) was treated with $Eu(fod)_3d_{30}$, it was possible to separate the single methylene signal representing four protons at 2.0 - 2.2δ into two distinct multiplets of equal intensity. Since the shift reagent would be expected to complex with the azo group, the protons <u>syn</u> to the azo group would experience a much larger downfield shift than the two protons which are <u>anti</u> relative to the azo group. When enough shift reagent to cause the chemical shift of the two bridgehead protons to appear at 10.1δ had been added, the methylene signals appeared as two multiplets centered at 4.1 and 5.1δ, respectively. Even greater separation could be achieved by the addition of more shift reagent or by lowering the temperature. As predicted, the downfield methylene signal was shifted to a much greater extent than the upfield methylene signal in these experiments.

While the azo compound CCCXXV (p 109) was a reasonably stable solid, it was found that it was impossible to prepare and isolate the unsaturated analog, CCCLII. When the Diels-Alder adduct, CCCXXVII (p 109), was treated with alcoholic KOH, a small amount of pleiadiene, CCCXXVI (p 109), was the only isolable product. One plausible explanation is that at least a small amount of Compound CCCLII did form but underwent a retro- Diels-Alder reaction to give CCCXXVI (p 109). Other examples of this behavior can be found in the chemical literature,[86] and other mechanisms should certainly be considered in this case.



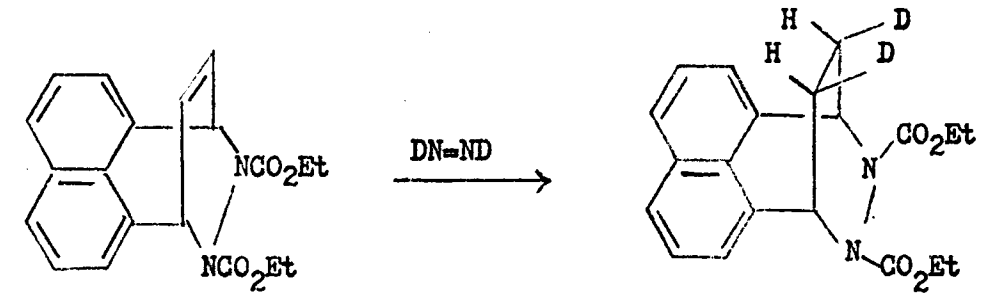
CCCXXVII CCCLII CCCXXVI

Another approach to CCCLII is via Compound CCCLIII, the Diels-Alder adduct of CCCXXVI (p 109) and di-tert-butyl azodicarboxylate. Once formed Compound CCCLIII could then be hydrolyzed under mild conditions, thereby allowing the isolation of CCCLII. Unfortunately, refluxing CCCXXVI (p 109) and di-tert-butyl azodicarboxylate for 18 hours in benzene gave only unreacted starting materials as did refluxing a mixture of CCCXXVI (p 109) and di-tert-butyl azodicarboxylate in xylene for 18 hours. In an attempt at effecting ester exchange, a sample of CCCXXVII (p 109) was refluxed for 8 hours in t-butyl alcohol with two equivalents of potassium t-butoxide. Nmr analysis of the product mixture showed that the ester groups had undergone no signifigant exchange. Similarly, attempts at catalyzing the reaction using anhydrous aluminum chloride and boron trifluoride etherate failed.



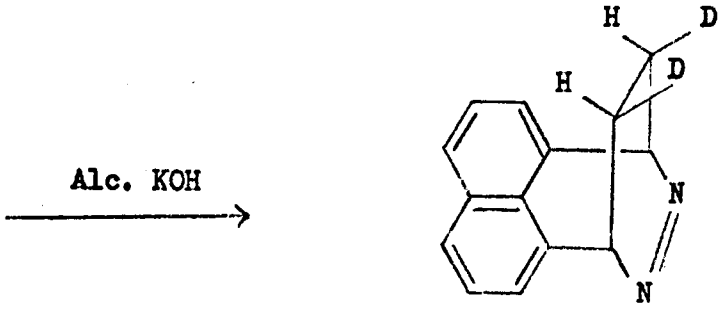
CCCLIII

In order to obtain stereochemical information about the mode of decomposition of CCCXXV (p 109), Compound CCCLIV was prepared by treatment of Compound CCCXXVI (p 109) with diimide-$\underline{d}_2$ followed by base hydrolysis. When the nmr spectrum of CCCLIV was compared to that of CCCXXV (p 109), it was found that the multiplet representing four protons at 2.1 - 2.6δ had diminished and now represented two protons while the rest of the spectrum was unchanged. From these data alone, it was impossible to determine the stereochemistry of the deuterium addition. Fortunately, a study of deuteriated azo compound, CCCLIV, with shift reagent was more successful.



CCCXXVII
CCCXXVII

CCCXXVIII-d_2



CCCLIV

The nmr spectrum of Compound CCCLIV is very similar to that of CCCXXV (p 109) except that the methylene peak at 1.0 - 2.2 represents only two protons. The addition of $Eu(fod)_3d_{30}$ to the sample caused no separation of the methylene peaks; thereby, indicating that the deuterium had added predominantly from one side. The addition of more shift reagent resulted in only a slight downfield

shift of the methylene signal. When enough shift reagent had been added to cause the bridgehead signal to appear at 10.1 , the methylene signal was located at 4.1 . This methylene signal corresponds exactly with the upfield methylene signal of Compound CCCXXV (p 109) under the same conditions. Thus, it appears from these experiments that the deuterium had added syn relative to the azo group. This conclusion is certainly not unexpected since anti addition of deuterium to Compound CCCXXVII (p 109) would be expected to be sterically hindered.

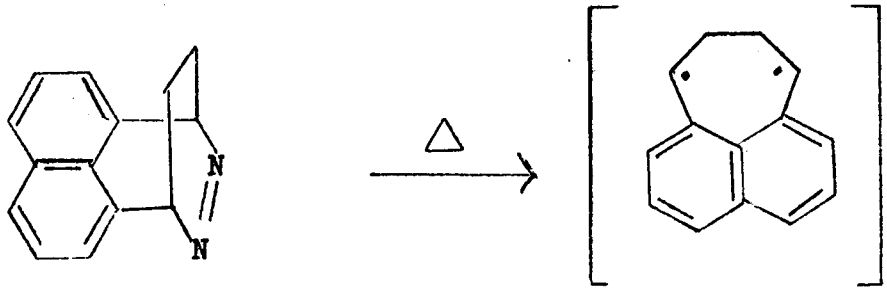
It should be noted that the assignment of hydrogens by the use of shift reagents may be misleading since there is both a distance dependence and an angular dependence on the magnitude of the observed shift of a hydrogen in relation to the site of complexation. However, even if the assignments in this case are completely wrong, there will be no effect on the conclusions drawn from the decomposition experiments as will be demonstrated later.

C. Thermal and Photochemical Studies

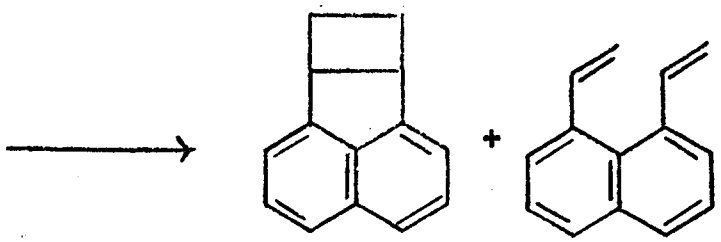
After a practical synthetic route to CCCXXV (p 109) had been established, an adequate quantity of this azo precursor to CCCXXIV (p 108) was prepared and a study of its thermal behavior was undertaken. As stated earlier (p 120) Compound CCCXXV (p 109) was found to be a relatively stable crystalline solid at room

temperature. This behavior is in direct contrast to that of other cyclic and bicyclic azo compounds such as CCX (p 74), CCXX (p 78) and CCXXII (p 78).[70]

The initial tasks were to determine the conditions necessary for the thermolysis of CCCXXV (p 109), to isolate and identify the products, and to elucidate the kinetic parameters. The decomposition of CCCXXV (p 109) was carried out in degassed tetrachloroethylene at 134.0° and monitored by nmr. At this temperature CCCXXV (p 109) completely disappeared and only two new products were observed and subsequently isolated. It was found that the reaction products could be separated on a 5% silver-nitrate silica gel column and the two products were identified as 1,8-naphthocyclobutane, CCCLV, and 1,8-divinyl-naphthalene, CCCLVI. The ratio of CCCLV to CCCLVI formed in this reaction was 7:1 and the reaction products isolated were identical to CCCLV and CCCLVI prepared by independent methods.[95,96,111]



CCCXXV CCCXXIV



(120)

CCCLV CCCLVI

It should be noted that CCCLV and CCCLVI were the only products obtained and that other products such as dimeric or polymeric materials were not observed. In control experiments authentic samples of CCCLV and CCCLVI in degassed tetrachloroethylene were heated at 134.0° for periods up to four hours. It was found that these compounds were completely stable at this temperature and that they did not interconvert or decompose under the reaction conditions.

In an effort to determine the multiplicity of the reaction intermediate, additional thermal experiments were carried out in a variety of solvents and these results are summarized in Table IV. In no case was any product of hydrogen or chlorine abstraction, dimerization or solvent addition observed. All of these results point to a singlet or unquenchable triplet. If the intermediate were a triplet species as usually encountered it should have behaved far differently. Certainly chlorine abstraction in carbon tetrachloride

TABLE IV

PRODUCT DISTRIBUTION FROM PYROLYSIS

Reactant	Solvent	T	CCCLVI/CCCLV[a]	CCCLVIII/CCCLIX	CCCLXI/CCCLXII
CCCXXV	Methanol	134°	0.12		
CCCXXV	Tetrachloroethylene	134°	0.14		
CCCXXV	Hexafluorobenzene	134°	0.14		
CCCXXV	Cyclohexane	134°	0.15		
CCCXXV	Carbon Tetrachloride	134°	0.14		
CCCXXV	Benzene	134°	0.22[b]		
CCCXXV	Ethyl Iodide	134°	----[b]		
CCCXXV	1-Chloronaphthalene	140°	0.21		
CCCXXV	Diethyl Maleate	134°	----[c]		
CCCXXV	Diethyl Fumarate	134°	----[c]		
CCCLIV	Carbon Tetrachloride	134°	0.15	1.2[d]	1.0
CCCXXV	$CH_3O_2CC\ CCO_2CH_3$	134°	----[c]		

[a]All product and deuterium ratios were determined by nmr.

[b]The ethyl iodide was unstable under the reaction conditions.

[c]It was not possible to determine accurate product ratios.

[d]The ratio is unity within the accuracy of the measurement.

and hydrogen atom abstraction in methanol could be reasonably expected to be observed if a long-lived triplet intermediate were involved. Further, the formation of dimers would have been expected from a long-lived triplet in the relatively concentrated solutions employed. Running the reaction in pure diylophiles such as diethyl fumarate diethyl maleate, and dimethyl acetylenedicarboxylate should by all accounts trap a quenchable triplet or singlet. However, as can be seen in Table IV (p 127), the diylophiles failed to react with the intermediate or alter the reaction or product distribution in any way relative to the other solvents employed in the study. That is, the only observed products were Compound CCCLV (p 126) and CCCLVI (p 126) formed in an approximate ratio of 7:1. A somewhat surprising result is that the product ratios listed in Table IV (p 127) are all essentially identical regardless of the nature of the solvent employed. This result indicates that the intermediate is unaffected by solvent properties or that the intermediate has such a short intrinsic lifetime under the reaction conditions that it reacts before solvent effects can become operative. When the decomposition of CCCXXV (p 109) was carried out in degassed iodobenzene, degassed hexafluorobenzene, and 1-chloronaphthalene in air, the only products were again CCCLV (p 126) and CCCLVI (p 126). These products were formed in essentially the same ratio as with any of the other solvents employed. Carrying out the decomposition in the above three solvents would be expected to facilitate the interconversion of an excited state singlet to a ground state triplet through the enhancement of spin-

orbit coupling.[3] Again, if a triplet had been involved, the formation of dimers would have again been expected, but they were not observed. It may be concluded from the results that the reaction proceeds by the same mechanism in these solvents as in the solvents mentioned earlier.

In an attempt to capture the reaction intermediate, a sample of Compound CCCXXV (p 109) was heated at 134° in the presence of tetracyanoethylene. Under these conditions only an intractable charge-tansfer complex was formed and no trapped intermediate, CCCLV (p 126) or CCCLVI (p 126), could be detected in the nmr spectrum of the reaction mixture.

Table V summarizes the results obtained when Compound CCCXXV (p 109) was irradiated with 3500Å light at room temperature in a wide variety of solvents. As was the case in the thermal reaction the photochemical decomposition of CCCXXV (p 109) exhibited a remarkable insensitivity to solvent and the only observed products were CCCLV (p 126) and CCCLVI (p 126) which were formed in a ratio of approximately 7:1 regardless of the particular solvent employed. These results suggest that the same intermediate is involved in both the thermal and photochemical decompositions of Compound CCCXXV (p 109). Further, no dimers or product of hydrogen or chlorine abstraction from the solvent were ever observed. Carrying out the photolysis in the presence of diylophiles such as diethyl fumarate, diethyl maleate or dimethyl azodicarboxylate, gave only CCCLV (p 126) and CCCLV (p 126) and in the same ratio as obtained in the other solvents. Also,

TABLE V

PRODUCT DISTRIBUTION FROM PHOTOLYSIS WITH 3500Å IRRADIATION

Reactant	Solvent	T	CCCLVI/CCCLV[a]	CCCLVII/CCCLIX	CCCLXI/CCCLXII
CCCXXV	Methanol	20°	0.15		
CCCXXV	Tetrachloroethylene	20°	0.24		
CCCXXV	Hexafluorobenzene	20°	0.12		
CCCXXV	Cyclohexane	20°	---[b]		
CCCXXV	Carbon Tetrachloride	20°	0.16		
CCCXXV	Benzene	20°	0.11		
CCCXXV	Iodobenzene	20°	0.25		
CCCXXV	Ethyl Iodide	20°	----[c]		
CCCXXV	Methylene Chloride	- 77°	0.02		
CCCXXV	Methanol	- 77°	0.02		
CCCXXV	Methylene Chloride	-196°	0.02		
CCCLIV	Carbon Tetrachloride	20°	0.18	0.9[d]	0.8[d]
CCCLIV	Ethanol Glass	-196°	2.5	1.1[d]	1.0

[a]All product and deuterium ratios were determined by nmr.

[b]The ratio could not be determined accurately.

[c]The ethyl-iodide was unstable under the reaction conditions.

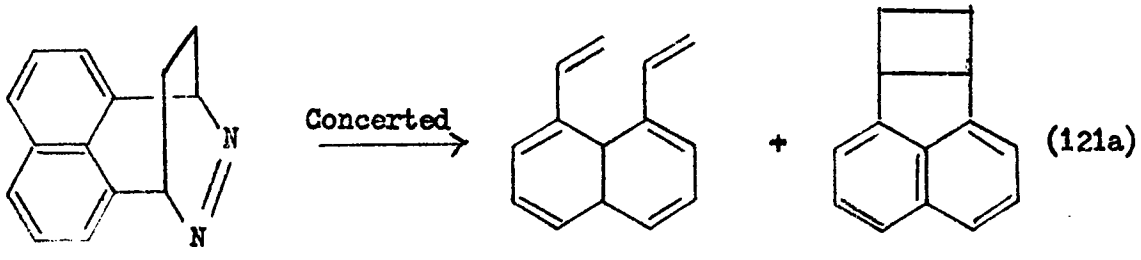
[d]The ratio is unity within the accuracy of the measurement.

carrying out the photolysis in solvents such as degassed hexafluoro benzene and iodobenzene and 1-chloronaphthalene in air which would be expected to facilitate the interconversion of an excited state singlet to a ground state triplet gave no change in the observed products or their relative ratios. In another attempt at facilitating the $T_1 \longleftarrow S_0$ transition by the heavy atom effect, Compound CCCXXV (p 109) was photolyzed in ethyl iodide at room temperature. Unfortunately, this experiment failed due to the apparent photolytic instability of the ethyl iodide and no useful data were obtained.

When the photolysis of CCCXXV (p 109) was carried out in methylene chloride or methanol at -77° the ratio of CCCLVI (p 126) to CCCLV (p 126) became quite large. However, when the photolysis of CCCXXV (p 109) was carried out in ethanol glass at $77^{\circ}K$, the major product was 1,8-divinylnaphthalene. This radical difference in the photochemical product ratios provides a signifigant insight into the mechanism of the reaction and will be discussed later. Control experiments were carried out on CCCLV (p 126) and CCCLVI (p 126) and they were found to be completely photostable under the reaction conditions and did not interconvert. Further, the photolyses were monitored as a function of time by nmr and the ratio of CCCLV (p 126) to CCCLVI (p 126) was invariant throughout the duration of a given experiment. Thus, the observed products are the initial products in the photolysis of CCCXXV (p 109).

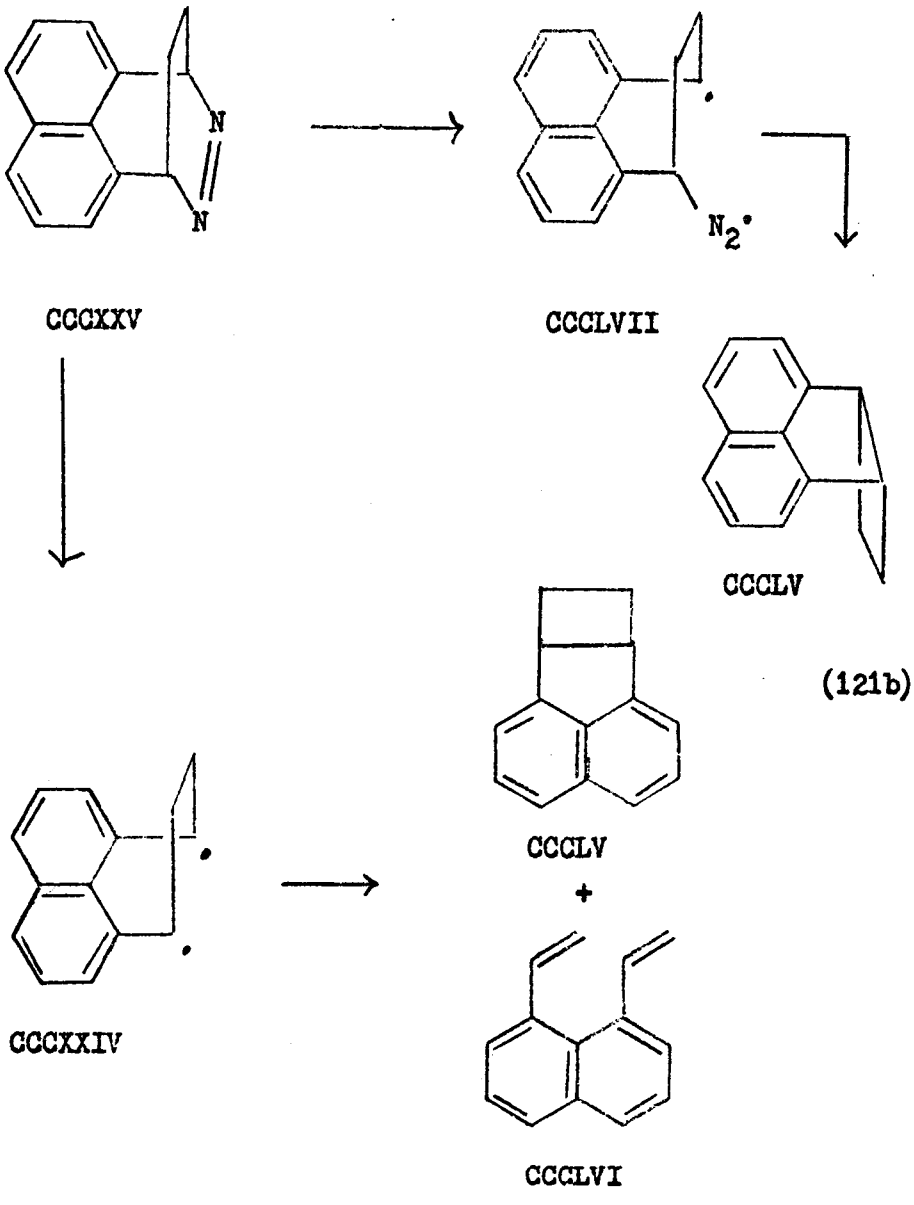
Thus far very little has been said about the nature of the

intermediate in the thermal and photochemical decompositions of Compound CCCXXV (p 109). Certainly the existence of the quinodimethane, CCCXXIV (p 109), has not been demonstrated. The most obvious explanation is, of course, that these reactions do not involve an intermediate at all and that Compounds CCCLV (p 126) and CCCLVI (p 126) are produced directly in a totally concerted decomposition of CCCXXV (p 109). Another possibility is that a stepwise elimination of nitrogen is occurring as illustrated in Equation 121b. If a one-step concerted mechanism is involved, the reaction should be highly stereospecific as would be the case if the step-wise elimination were involved (see Equation 59 (p 64)). However, if either singlet or triplet CCCXXIV (p 109) were an intermediate, the reaction would probably not be stereospecific since the diradical would probably be able to equilibrate before the product was formed.



(121a)

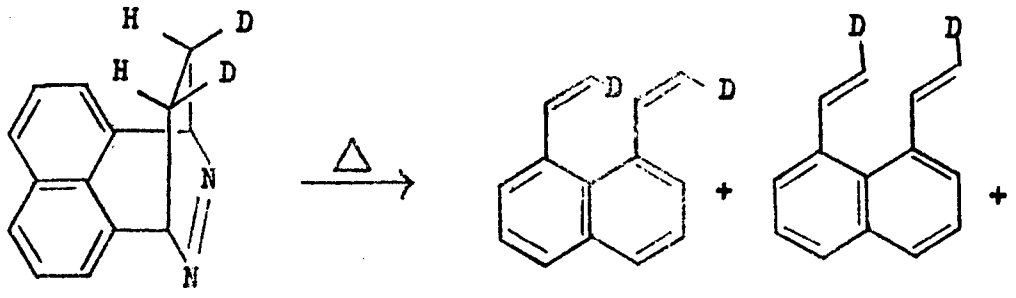
CCCXXV CCCLVI CCCLV



(121b)

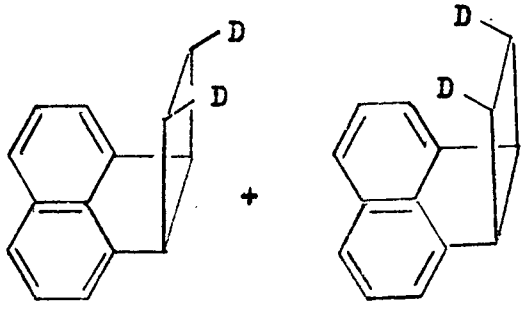
In order to resolve this question and perhaps provide additional stereochemical information, Compound CCCLIV (p 124),

was prepared as described earlier in this chapter. A sample of CCCLIV (p 124) was heated in degassed carbon tetrachloride at 134.0° and monitored by nmr. As in the thermolysis of CCCXXV (p 109) the only products observed were 1,8-divinylnaphthalene and naphthocyclobutane. Further, as would be expected, they were formed in the same ratio as observed in the thermolysis of CCCXXV (p 109), Table IV (p 127). Nmr analysis of the products indicated that the deuteriated naphthocyclobutane consisted of a 50:50 mixture of anti, cis-dideuterionaphthocyclobutane, CCCLVIII, and syn, cis-dideuterionaphthocyclobutane, CCCLIX. While its formation would be unexpected, no trans-dideuterionaphthocyclobutane, CCCLX, was formed as shown by the nmr. Similar analysis of the 1,8-divinylnaphthalene product showed the deuterium label to be equally distributed between the two available sites on the terminal methylenes thus giving a 50:50 mixture of cis and trans product. Note that nmr could not distinguish a 50:50 mixture of cis, cis-dideuterio-1,8-divinylnaphthalene, CCCLXI, and trans, trans-dideuterio-1,8-divinylnaphthalene, CCCLXII, from 100% of cis, trans-dideuterio-1,8-divinylnaphthalene, CCCLXIII, since there is no coupling between the protons of the adjacent vinyl groups.

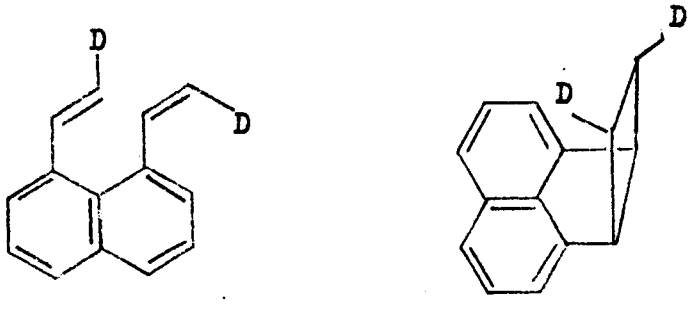


CCCLIV CCCLXI CCCLXII

(122)



CCCLVIII CCCLIX



CCCLXIII CCCLX

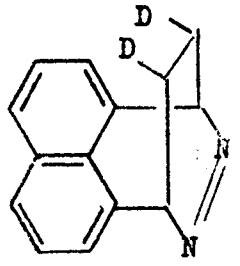
Compound CCCLVIII (p 135) was prepared by the diimide-d_2 reduction of Compound CCCXXXIV (p 110) and was found to be completely stable under the reaction conditions and showed no evidence of label scrambling. Nelsen and Gillespie have previously prepared Compound CCCLXII (p 135) and had demonstrated that after heating at 350° the recovered 1,8-divinylnaphthalene contained only 10% cis label.[95] It is clear that a negligible amount of label scrambling would occur with the much lower temperatures used in the present study. Thus, the observed product ratios and deuterium distributions accurately reflect the initially formed products.

Compound CCCLIV (p 123) was then irradiated in degassed carbon tetrachloride at room temperature using 3500Å light. Nmr analysis of the products showed 1,8-divinylnaphthalene and naphthocyclobutane with the same deuterium distribution as was obtained thermally, Table IV (p 127). Compound CCCLVIII (p 135) was found to be completely photostable under the reaction conditions by control experiments. Although no specifically labelled 1,8-divinylnaphthalene was available for this study, Compound CCCLVI (p 126), does not absorb 3500Å light appreciably and any CCCLXI (p 135), CCCLXII (p 135) or CCCLXIII (p 135) formed should be photostable under these conditions. Therefore, it is reasonable to assume that the deuterium distribution in this case is again the initial one.

As stated previously, irradiation of CCCXXV (p 109) in ethanol glass at 77°K gave the same products produced in the photolysis of fluid solutions; however, their distribution was drastically

different. Obviously, the deuterium distribution in the photolysis products of CCCLIV (p 123) in ethanol glass could be quite informative. When this experiment was carried out the product distribution was again quite different from that obtained in fluid solution, Table V (p 130); however, the deuterium distribution in each of the products was identical to that obtained in fluid solution, Table V (p 130).

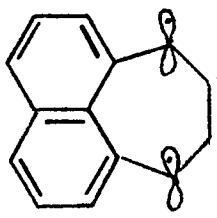
At this point it is appropriate to note that if the assignment of the stereochemistry of CCCLIV (p 123) had been totally incorrect as discussed earlier, the observed results would have been unaltered. This is due to the complete randomness of the deuterium label in both products which indicates that either CCCLIV (p 123) or CCCLXIV would be expected to give the same result.



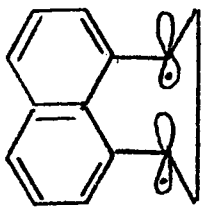
CCCLXIV

The net result of these stereochemical studies is that CCCXXIV (p 108) is indeed an intermediate in both the thermal and photochemical decomposition of CCCXXV (p 109). The deuterium distribution observed in the products is incompatible with either a

single-step concerted reaction or a nitrogen biradical such as CCCLVII (p 133). Indeed CCCXXIV (p 109) behaves as if it were flat although molecular models indicate that this conformation is highly strained. In addition to the planar conformation of CCCXXIV (p 109) (C_{2v} symmetry), the skew conformer (C_i), an equilibrating mixture of boat conformers, (C_s), or a combination of any or all of these conformers is capable of accommodating the deuterium distribution.



CCCLXV, C_{2v}



CCCLXVI, C_i



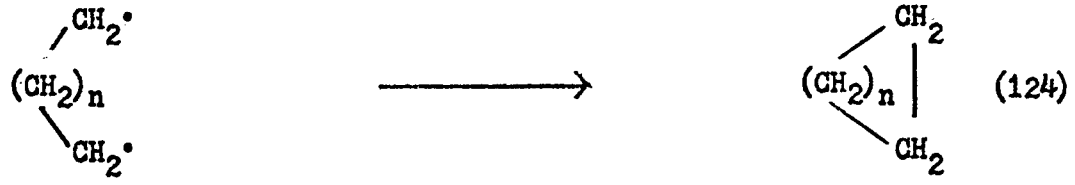
CCCLXVII, C_s

D. Chemically Induced Dynamic Nuclear Polarization (CIDNP) Studies

Recently, chemically induced dynamic nuclear polarization (CIDNP) has been used to detect the presence of triplet biradicals[78]

and has been used with great success to elucidate the mechanisms of carbanion rearrangements.[112,113] This technique is extremely sensitive and is capable of detecting even a minute quantity of triplet biradicals in a reaction. The extreme sensitivity of CIDNP as a radical detection device is a result of the dependence of the phenomenon on net spin polarization of nuclei in intermediates and products and not totally on the instantaneous concentration of any given species. The pyrolysis of samples of CCCXXV (p 109) in degassed 1-chloronaphthalene was carried out directly in the nmr probe at 145° and 200° ($t_{\frac{1}{2}} < 5$ min) over an extended time period. At no time during either of the experiments was any CIDNP observed; however, it is not clear whether a CIDNP should be observed at all in the decomposition of CCCXXV (p 109), even if a triplet was involved.[4]

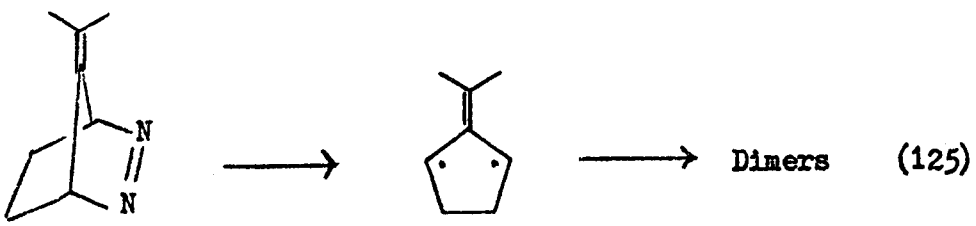
The used of CIDNP in the study of the intramolecular reactions of biradicals is severely limited in that CIDNP will be observed in the conversion of Compound CCCLXVII to CCCLXIX when n is large. However, when n is small such as in 1,3 and 1,4 biradicals (where n=1,2, respectively) no CIDNP is found.[114] In the case of CCCXXIV (p 108), the two nonbonded π electrons are not only close physically (n = 2) but they are also part of the same π system and therefore, must undergo extensive interaction. On this basis enhanced nmr signals for CCCLV (p 126) and CCCLVI (p 126) would not be expected when CCCXXV (p 109) is thermally decomposed in an nmr probe.



(124)

CCCLXVIII CCCLXIX

As previously discussed (p 39), Berson and co-workers observed a CIDNP in the dimers formed in their study of the decomposition of LXII (p 32). These dimeric products are formed, at least in part, from the triplet intermediate LXI (p 32) as seen by CIDNP.[115] By analogy, the remarkable sensitivity of CIDNP might conceivably allow the observation of triplet derived dimers of CCCXXIV (p 108) formed in concentrations too low to be detected by other means. Unfortunately the experimental results showed no evidence of CIDNP and no conclusions concerning the electronic nature of CCCXXIV (p 108) could be made.



(125)

LXII LXI LXIII-LXVI

E. Electron Spin Resonance

In order to elucidate the electronic nature of the intermediate CCCXXIV (p 108), electron spin resonance experiments were carried out by Dr. J. R. Dodd of Emory University.

A 0.15M solution of Compound CCCXXV (p 109) in hexafluorobenzene at -160° was irradiated inside an optical transmission esr cavity. After several minutes of irradiation, the esr spectrum shown in Figure 5 was obtained. This spectrum exhibits resonance lines which are characteristic of a randomly oriented triplet species as well as a stronger resonance near g = 2 which is attributable to a radical species. With 9.221 GHz microwave radiation, resonance lines are observed at 3088 and 4380G and at 3192 and 3375G and are assigned, respectively, to the signals of a randomly oriented triplet state of CCCXXIV (p 108) oriented perpendicular and parallel to the magnetic field and having an axially symmetric or nearly axially symmetric spin distribution. The $\Delta M = \pm 2$ transition for the triplet is quite weak but observable under high gain and modulation at 1640G. The zero field splitting parameters for CCCXXIV (p 108) are $|D| = 0.018cm^{-1}$ and $|E| \leq 0.003cm^{-1}$. The observation of only four triplet resonances in the high field portion of the triplet spectrum indicates that $|E|$ is nearly zero and in this case the linewidth of the inner pair of triplet resonances can be taken as a limit for $|E|$.

One might reasonably ask if the triplet signal is really due

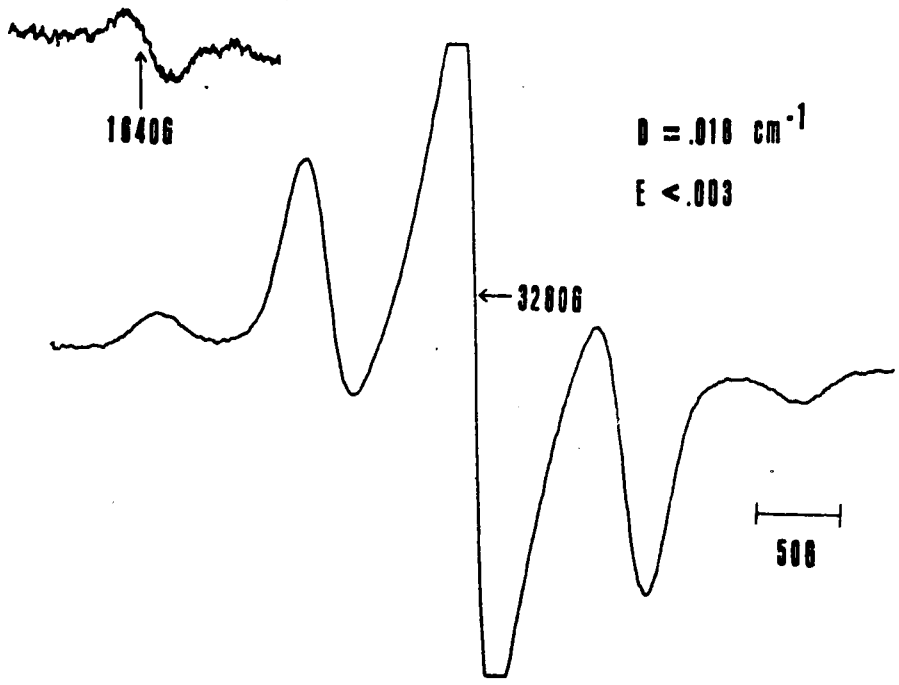
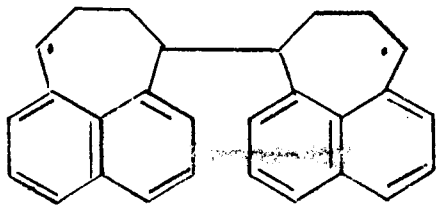


Figure 5. ESR of Triplet CCCXXIV (p 108).

to CCCXXIV (p 108) or to some other radical intermediate. It is conceivable, if not likely, that the triplet signal is due to a dimer such as CCCLXXI or perhaps an even higher aggregrate of CCCXXIV (p 108). If this were the case, the triplet signal should rapidly diminish or change when the concentration of CCCXXV (p 109) is lowered. Experimentally, no change in the triplet signal whatsoever was observed when the concentration of CCCXXV (p 108) in hexafluorobenzene was varied from 0.15M to 6.87×10^{-3}M, a twenty-fold difference.



CCCLXXI

In order to determine whether CCCXXIV (p 108) has a triplet ground state or if it has a singlet ground state accompanied by a thermally accessible triplet state, the intensity of the triplet esr absorption was studied as a function of temperature. If CCCXXIV (p 108) has a ground state triplet, the intensity (I) of the triplet absorption will vary inversely with the absolute temperature and as a result the product IT will remain constant as the temperature is varied. This is simply a statement of the Curie law. Conversely,

if the observed triplet is not the ground state of the molecule, but instead is of an energy ΔE above the ground state, then the intensity of the triplet signal will change as the population of the excited triplet state changes. Thus, in the present case, the product IT will increase as the temperature increases and Equation 126 will be followed.

$$IT = (e^{-\Delta E/RT})/(1+3e^{-\Delta E/RT}) \qquad (126)$$

The intensity of the triplet resonance lying to the left of the g = 2 radical absorption was measured as a function of temperature over the range -140° to -177°. The peak to peak height of the resonance line was taken as a measure of the intensity of each temperature since the linewidth of the resonance line was observed to remain constant over the temperature range investigated. Unfortunately an irreversible decay of CCCXXIV (p 108) in this temperature range was detected and, as a result, changes in the intensity of the triplet resonance were not completely reversible. In order to correct for intensity changes due to the decay of CCCXXIV (p 108), the sample was immediately cooled to -177°, where the irreversible decay was very slow, after each intensity measurement at a given temperature. The intensity of the resonance line was then measured at -177° after allowing for temperature equilibration. In this manner it was possible to compare the intensity of the resonance

at a given temperature with the intensity of the line at -177° within a very short time, thereby, making any differences in intensities due to decay of CCCXXIV (p 108) negligible. Further it should be noted that the intensity of the triplet signal was completely reversible if the temperature changes occurred over a short time period.

Experimentially the product IT was found to increase by 14.8% in going from -177° to -140°. In contrast, the IT product for the radical absorption (where the paramagnetic state is the ground state) was constant within experimental error (maximum variation 2.7%). The results of this study indicate that the observed triplet state of CCCXXIV (p 108) is not the ground state but rather a low-lying thermally accessible triplet state.

It is possible to calculate the energy difference (ΔE) between the singlet ground state and the triplet excited state in the following manner. The ratio $(IT)_T/(IT)_{-196^\circ}$ could be calculated from the experimental data for various temperatures. These values could then be compared to the same ratios calculated from Equation 126 (p 143) using selected values for ΔE. When this procedure is carried out, the best fit of the experimental and theoretical ratios occurs when $\Delta E = 200$ cal/mole. Thus, the observed triplet state of CCCXXIV (p 108) lies approximately 200 cal/mole above the singlet ground state.

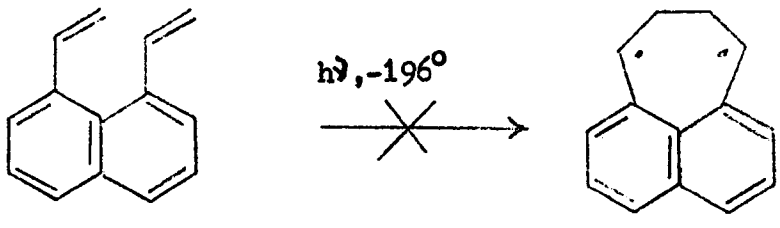
As stated previously triplet CCCXXIV (p 108) was observed to undergo irreversible decay at -130°. The initial half-life was 18

minutes; however, the decay was not a first order process. That is, the decay rate was quite fast initially but this rate tapered off as a function of time (the second half-life was approximately 47 min.). A plausible explanation for this observation is that the decay rate is reflecting multiple pathways for CCCXXIV (p 108). The initial rapid decay most probably occurs via process in which CCCXXIV (p 108) abstracts an atom, perhaps a hydrogen atom, from trace hydrocarbon impurities in the solvent, to form a radical species. That this process is indeed occurring is supported by the significant increase in the intensity of the g = 2 radical resonance at the same time that the triplet intensity was decreasing. Since the solution is a rigid matrix, other molecules of CCCXXIV (p 108) may not be located at a suitable distance or with a suitable orientation to abstract an atom from a donor molecule; in this instance the mode of decay may involve a slower unimolecular decay in which CCCXXIV (p 108) is converted into one or both of the observed products.

In another experiment, Compound CCCXXV (p 109) was irradiated in an ethanol glass and the same triplet was observed in the esr spectrum as was observed in hexafluorobenzene. The only signifigant difference between the two spectra was the greatly reduced amount of the radical near g = 2 seen in the ethanol glass. The observation of the triplet in the ethanol glass is particularly intriguing since, as already noted, both CCCLV (p 126) and CCLVI (p 126) are formed under the same experimental conditions when Compound CCCXXV (p 109) is photolyzed. Thus, at least a portion of the overall reaction

proceeds through a triplet electronic state of CCCXXIV (p 108), although the amount of reaction proceeding through this triplet is not known since it is not possible to correlate the intensity of the esr signal with the amount of quinodimethane present.

Another possible approach to this observable electronic state of CCCXXIV (p 108) is provided by the work of Meinwald, et al., who have shown that irradiation of 1,8-divinylnaphthalene, CCCLVI (p 126) affords two products.[117] One of these is the naphthocyclobutane, CCCLV (p 126), and this photoisomerization may proceed via the excited state of CCCLV (p 126). As a result of this, irradiation of CCCLVI (p 126) in ethanol glass might be a source of triplet CCCXXIV (p 108). When the esr experiment was carried out, no signals of any kind were observed. Further, when an ethanol glass containing CCCLVI (p 126) was irradiated for three hours at liquid nitrogen temperature using 3500Å radiation, only unreacted CCCLVI (p 126) was obtained. A plausible explanation for this apparent unreactivity is that the divinylnaphthalene probably exists in a conformation in the rigid medium in which the terminal carbon atoms cannot reach each other to form CCCXXIV (p 108).



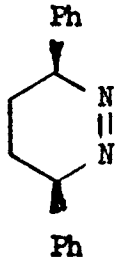
CCCLVI CCCXXIV (127)

F. Kinetic Parameters

At this point it was desirable to elucidate the kinetic parameters of the thermal decomposition in order to help reveal the mechanism. The thermal decomposition of CCCXXV (p 109) was found to follow first order kinetics as expected. The kinetic results were obtained by monitoring the $n \longrightarrow \pi^*$ transition (λ_{max} = 4110Å, ε = 1065) of solutions of CCCXXV (p 109) in degassed tetrachloroethylene (maintained at the desired temperature) as a function of time. Kinetic runs were carried out at 128.8°, 134.0° and 145.0° and the respective rate constants are presented below.

Temperature	k, sec^{-1}
128.8°	1.88×10^{-4}
134.0°	2.96×10^{-4}
145.0°	7.41×10^{-4}

An Arrhenius plot was carried out using the above three rate constants and E_a was found to be 28.7 ± 0.3 kcal/mole. This value is in line with the E_a expected for an α,α-diaryl cyclic azo compound (cf., CCCLXX, E_a = 27.3 kcal/mole).[116]



CCCLXX

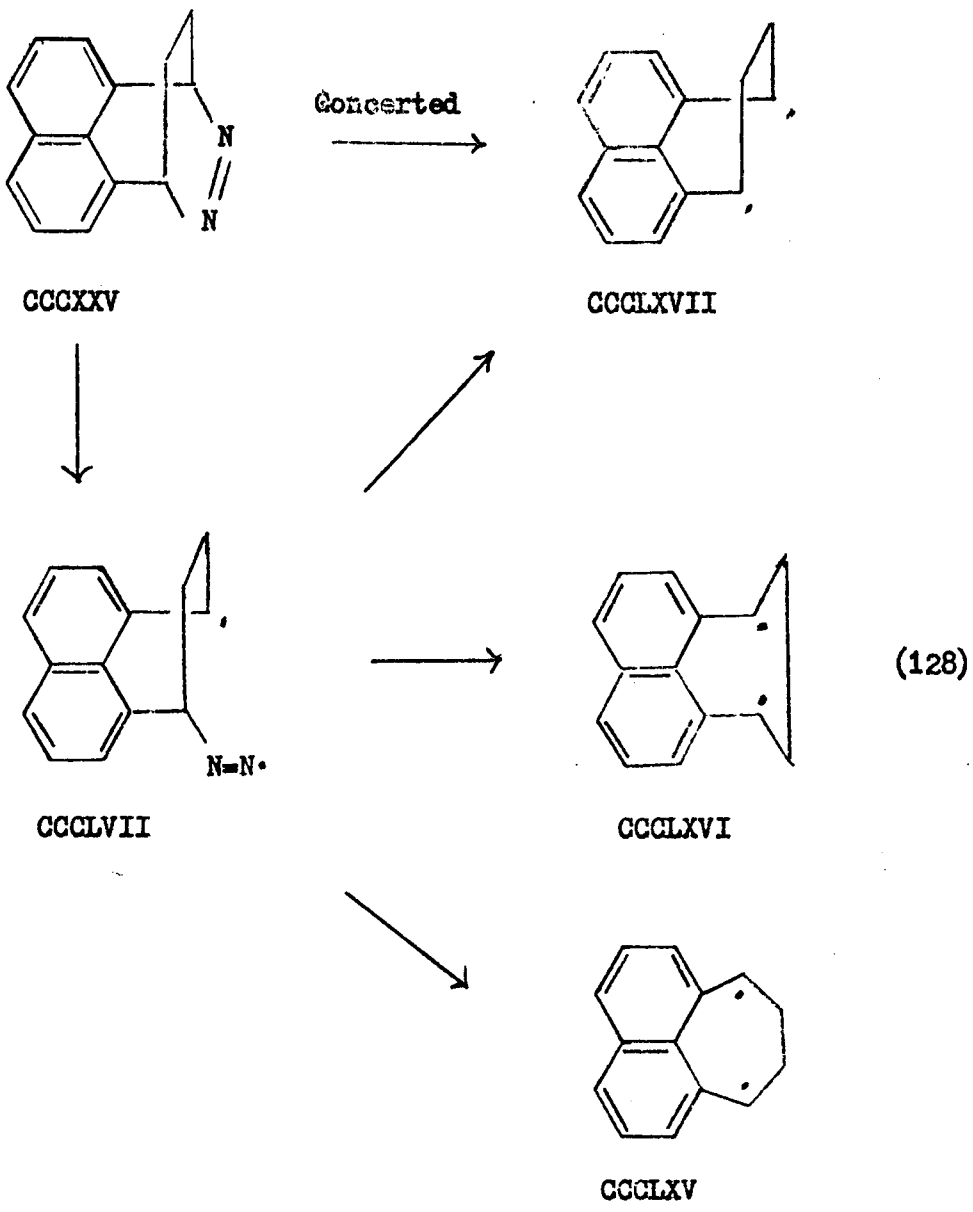
The $\Delta S^{\ddagger}$ (134.0°) calculated for CCCXXV (p 109) using the above data was found to be -6.7 ± 0.6 eu. This negative value for $\Delta S^{\ddagger}$ indicates a highly ordered transition state for the reaction and would be compatible with a concerted thermal decomposition of CCCXXV (p 109). In comparison the thermal decomposition of XLIII (p 24) to give trimethylenemethane, XLVI (p 24) a known ground state triplet, has a $\Delta S^{\ddagger}$ = -1.1 eu. The negative $\Delta S^{\ddagger}$ for this reaction has been attributed to the low probability of direct formation of triplet trimethylenemethane by a spin forbidden process.[33] A reasonable conjecture is that the above argument may be applied to the formation of CCCXXIV (p 108) from CCCXXV (p 109).

G. Conclusions

Having presented the evidence in the preceding text, it is appropriate to attempt to formulate a single, coherent mechanism which is capable of accomodating the data and accounting for the formation of CCCLV (p 126) and CCCLVI (p 126) from CCCXXV (p 109). As a result of the stereochemical studies it was conclusively demonstrated that CCCXXIV (p 108) was in fact an intermediate in both the thermal and photochemical decomposition of CCCXXV (p 109); however, it was also shown that CCCXXIV (p 108) is capable of existing in at least three distinct conformations each of which will have both a singlet and triplet electronic state. An additional complication is that any one of these singlet and triplet conformers

may interconvert and then isomerize to either one or both of the observed products. Thus, even assuming a minimum of three conformers for CCCXXIV (p 108), there are a vast number of pathways available by which CCCXXIV (p 108) can form CCLV (p 126) and CCCLVI (p 126) and still accommodate the data. Fortunately, it is possible to produce a reasonable scheme which adequately explains the experimental results by the judicious use of MO calculations, the principle of least motion and consideration of orbital overlap.

The initial task in the data correlation is to elucidate the mode of nitrogen expulsion for CCCXXV (p 109) in both the thermal and photochemical decompositions. The only methods available for nitrogen expulsion in this instance are a concerted process and a step-wise process. If nitrogen is lost is a concerted reaction, only the bent conformer, CCCLXVII, would be formed directly while a stepwise loss would give an intermediate which could decay to give any one or all of the possible conformers. As stated earlier (p 148) the E_a for the decomposition of CCCXXV (p 109) is 28.7 $\pm$ kcal/mole, and this is a reasonable result for an α,α-diaryl cyclic azo compound. Unfortunately this reveals nothing about the actual mechanism of the reaction. The $\Delta S^{\ddagger}$ (134.0°) was found to be -6.7 $\pm$ 0.6 eu and, as discussed previously, is very strong evidence for a concerted loss of nitrogen in the thermal reaction especially when it is compared to similar data for known ground state triplets.



CCCXXV CCCLXVII

CCCLVII CCCLXVI CCCLXV

(128)

In spite of the evidence in favor of a concerted loss of nitrogen in the thermal reaction, nothing can be said about the corresponding photochemical reaction. Fortunately, the manner in

which CCCXXV (p 109) loses nitrogen in either the thermal or photochemical reaction does not appear to have much bearing on the description of the dynamic behavior of CCCXXV (p 109). For example, if one were to assume that the reaction proceeds by the concerted loss of nitrogen, the bent conformer, CCCLXVII (p 138), would result and this conformer alone could account for only the formation of CCCLXIII (p 138), and CCCLXII (p 135) from CCCXXV (p 109); this deuterium distribution is contrary to the experimental results. Thus, even if CCCLXVII (p 138) were formed initially by the concerted process, it would have to interconvert to the other conformers of CCCXXIV (p 109) more rapidly than it isomerizes to product in order to give the observed deuterium distribution in the reaction products. Obviously, if the equilibration of the conformers is rapid, the same product and deuterium distribution will result regardless of the point of entry on the energy surface of CCCXXIV (p 108).

Examination of molecular models of the conformers of CCCXXIV (p 108) indicates that the twist and boat conformers are the most likely to be involved in these reactions. The planar conformer, CCCLXV (p 138), was intuitively eliminated on the basis of the large angle strain which would be expected to accompany a planar seven-membered ring. CNDO/2 and INDO calculation[118] were carried out on the singlet and triplet electronic states of each of the three conformers under consideration in order to give some substance to this intuitive assessment. A number of assumptions about the intermediates were necessary in order to carry out the calculations

since the actual bond angles and bond lengths of the conformers were obviously unknown. The model used assumed that the naphthalene moiety in each of the species investigated was unchanged from naphthalene itself. Further, the remaining bond angles and lengths were taken as those "normally" encountered in similar species. These calculations might be reasonably regarded with some suspicion since the model is at best crude and the use of CNDO/2 and INDO calculations on such large molecular systems is certainly questionable.[118] In spite of these objections, the results tabulated in Table VI consistently show the planar conformer, CCCLXV (p 138), to be significantly less stable for a given electronic state and method of calculation than CCCLXVI (p 138) and CCCLXVII (p 138). On the basis of these results it is reasonable to reject CCCLXV (p 138) as an intermediate in the decomposition of CCCXXV (p 109). Unfortunately, no such clearcut distinctions were possible for CCCLXVI (p 138) and CCCLXVII (p 138).

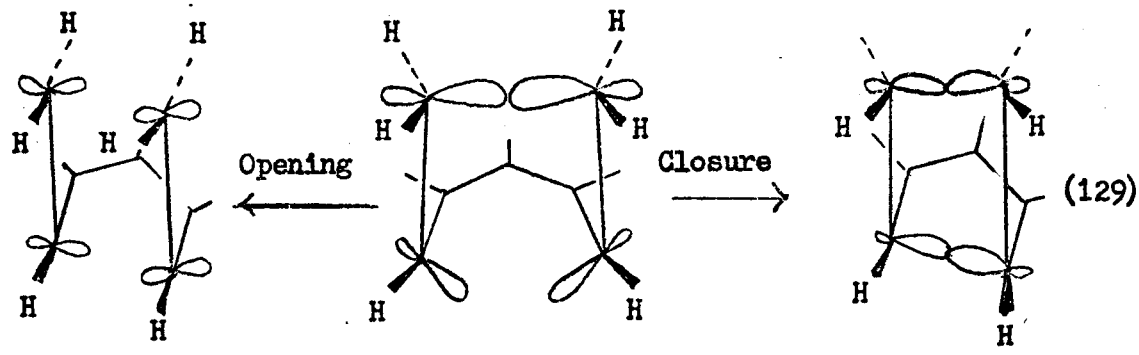
Examination of a molecular model of the boat conformer, CCCLXVII (p 138) reveals that the nonbonded orbitals on the methylenes attached to the C-1 and C-8 of the naphthalene ring face toward each other. Utilizing the principle of least motion, these orbitals can move toward each other and form a bond thereby giving rise to CCCLV (p 126). Note that these nonbonded orbitals are also aligned with the σ-bond which connects the two bridging methylene groups. As a result, it is possible for this σ bond to undergo stretching and subsequently break resulting in the formation of divinylnaphthalene

TABLE VI

CALCULATED BINDING ENERGIES (ATOMIC UNITS)

Method of Calculation	Electronic State	CCCLXV	CCCLXVI	CCCLXVII
CNDO/2	Singlet	-14.415	-14.671	-14.511
CNDO/2	Triplet	-14.582	-14.676	-14.658
INDO	Singlet	-14.146	-14.379	-14.247
INDO	Triplet	-14.246	-14.314	-14.323

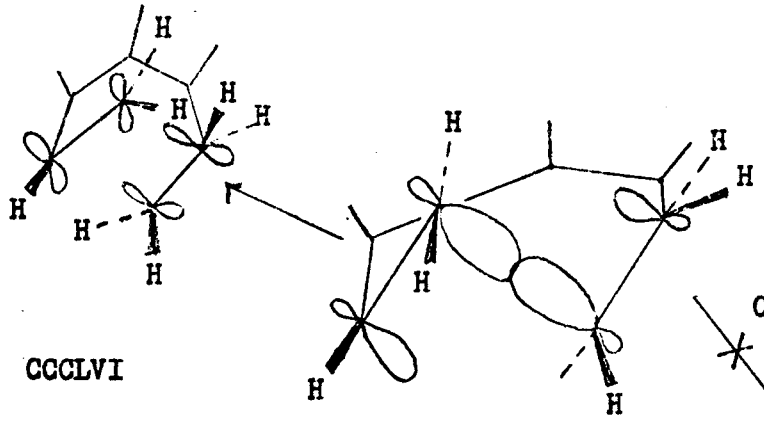
with only a minimal displacement of nuclei.



(129)

CCCLVI CCCLXVII CCCLV

When the twist conformer, CCCLXVI (p 138), is examined in a similar fashion, it can be seen that the nonbonding orbitals again overlap with the σ bond which joins the bridging methylenes although not to the extent found in CCCLXVII (p 138). Cleavage of this bridging bond would give divinylnaphthalene. Further, scrutiny of the model of CCCLXVI (p 138) reveals that naphthocyclobutane cannot be generated from the twist conformer directly. Thus, in order for CCCLV (p 126) to be formed, CCCLXVI (p 138) would have to be converted into CCCLXVII (p 138).



CCCLVI

CCCLXVI

(130)

Closure

CCCLV (p 126)

In summary, the above analysis implies that naphthocyclobutane can form from only the bent conformer while divinylnaphthalene can arise from either the bent or the twist conformer.

Using the above conformational analysis in conjunction with the information gained through the theoretical calculations, it is now possible to explain what occurs when the deuteriated azo compound CCCLIV (p 123) loses nitrogen. If one assumes that the nitrogen expulsion is a concerted process as indicated by the negative $\Delta S^{\ddagger}$, CCCLXVIIa will be formed. Conformer CCCLXVIIa can give rise to both of the observed products, but by itself cannot account for the observed deuterium distribution. However, if CCCLXVIIa could be rapidly converted into CCCLXVIIb, the correct deuterium distribution would result. The interconversion of CCCLXVIIa will be facile if the interconversion proceeds through CCCLXVIa. Alternately,

if CCCLXVIa were produced initially, 1,8-divinylnaphthalene would be the only product and in order for any naphthocyclobutane to be produced at all, CCCLXVIa must interconvert to CCCLXVIIa and CCCLXVIIb.

Several comments are in order regarding the above mechanism. As can be seen, the correct deuterium distribution will result only if CCCLXVIa, CCCLXVIIa and CCCLXVIIb are capable of equilibrating much more rapidly than they are converted into product. Further, if this conformational interconversion is rapid, the point of entry of a given reactant on the energy surface of CCCXXIV (p 108) will be of no consequence since CCCXXIV (p 108) will always yield the same ratio of products and deuterium distribution in these products. In addition there is at least a conceptual method available whereby the extent that CCCLVI (p 126) and CCCLXVII (p 138) open to produce 1,8-divinylnaphthalene can be discerned. As can be readily seen in Figure 6, a 50:50 mixture of CCCLXVIIa and CCCLXVIIb would form a 50:50 mixture of CCCLXII (p 135) and CCLXI (p 135) while CCCLXVIa would produce only CCCLXII (p 135). There is no obvious method by which a 50:50 mixture of CCCLXII (p 135) and CCCLXI (p 135) can be distinguished from 100% of CCCLXII (p 135). This point could be clarified if a label other than deuterium were employed and the isomers separated.

A similar mobile equilibrium has been proposed by Nelsen and Gillespie, who recently investigated the nmr temperature dependence of CCCLXXII and the esr spectra of the radical anions of CCCLXXII and CCCLXXIII. From their experimental results, they were able to

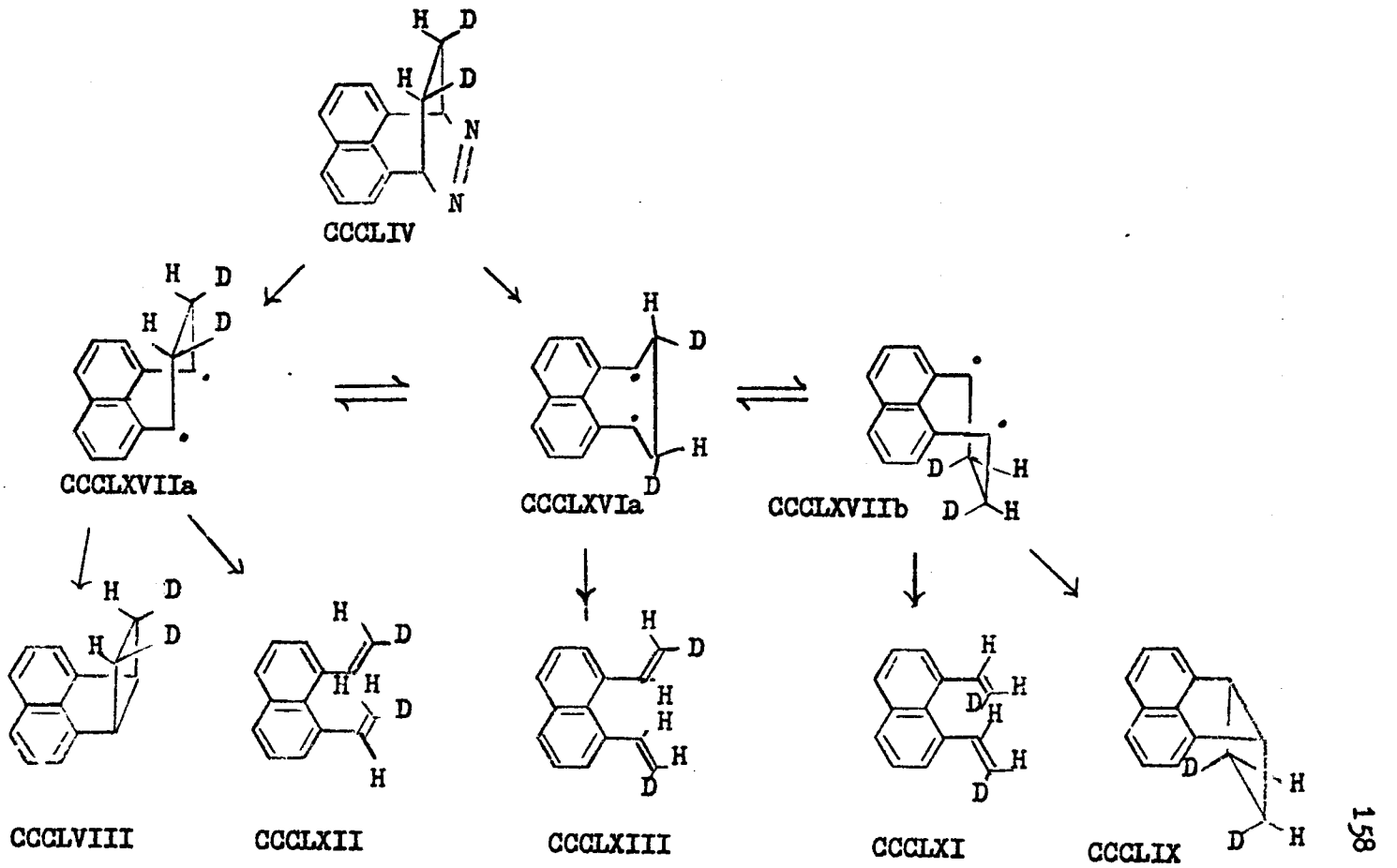
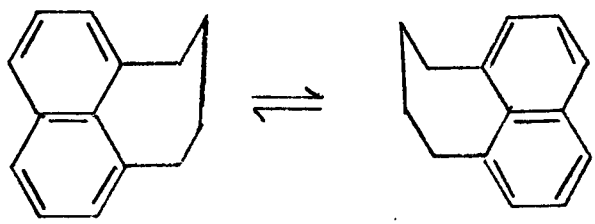
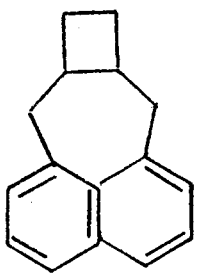


Figure 6. Proposed mechanism for the decomposition of Compound CCCLIV.

ascertain that CCCLXVIII exists primarily in the boat conformation and undergoes a rapid conformational interconversion presumably involving the twist conformer.



CCCLXVIII



CCCLXIX

In contrast with the above example in which the boat conformer is energetically more stable than the twist conformer, there is some experimental evidence which suggests that the twist conformer, CCCLXVI (p 138) at liquid nitrogen temperatures always gave 1,8-divinylnaphthalene, CCCLVI (p 126), as the major and sometimes the exclusive product. From the esr experiments it was observed that triplet CCCXXIV (p 108) decays very slowly under identical conditions. It is apparent then that, if the low temperature is maintained throughout

the photolysis, CCCXXV (p 109) will lose nitrogen to form CCCXXIV (p 108), but CCCXXIV (p 108) will not isomerize rapidly to products, CCCLV (p 126) and CCCLVI (p 126). As a direct result, the particular conformer of CCCXXIV (p 108) which is formed initially will be of no consequence since relaxation will eventually result in the formation of the most stable conformer assuming that ther is adequate space available for the conformational equilibration within the confines of the ethanol matrix. The most stable conformer in the ethanol matrix would have to be the twist conformer since it alone is capable of exclusive generation of Compound CCCLVI (p 126). If the most stable conformer in the ethanol glass had been the boat conformer, CCCLXVII (p 138), then Compound CCCLV (p 126) should have always been observed with Compound CCCLVI (p 126) and this was not the case. Assuming the above, the formation of CCCLV (p 126) in some of the low temperature photolyses can be explained in the following manner. Compound CCCLV (p 126) can form only from CCCLXVII (p 138) and the conversion of CCCLXVI (p 138) to CCCLXVII (p 138) is inhibited in the rigid medium. However, this process is rapid in liquid solution and once the matrix begins to thaw CCCLXVI (p 138) can be formed from CCCLXVI (p 138) and CCCLV (p 126) can then be generated. Fluctuations in the rate of thawing could then conceivably be responsible for the varying amounts of CCCLV (p 126) observed.

Assuming the above argument to be valid, the most stable conformer in the ethanol glass must also be responsible for the

triplet observed in the esr experiments. An interesting question to pose is why does this molecule have a singlet rather than a triplet ground state? Certainly any explanation on a molecular system this extensive is little more than conjecture; however, certain points merit consideration. As is the case with cyclobutadiene,[45] the Jahn-Teller effect can cause the singlet to be the lowest energy. This apparent reversal of the energy levels of the triplet and singlet electronic states is a result of a vibration or distortion of the correct symmetry. This distortion causes a splitting of the degenerate MO's at E = 0 which results in the singlet being the lowest energy state. In molecules having two electrons which are distributed over two degenerate MO's, the triplet will be the ground state only when the exchange integral for the two degenerate MO's is negative. When the exchange integral is positive, a singlet ground state will result even if distortions are absent as in the coronene dianion. Finally, if allowance is made for a weak interaction or overlap between the nonbonded orbitals on the radical centers, the degeneracy of the highest occupied molecular orbitals will be destroyed by splitting and a singlet ground state will result. This last concept is supported by Hückel calculations on CCCXXIV (p 108) and is a reasonable conjecture since the two radical centers must overlap to some extent due to their proximity.

At this point one can only speculate as to whether the conformers CCCLXV (p 138) and CCCLXVII (p 138) interconvert on a

triplet or singlet energy surface and from which electronic state do the products arise.

CHAPTER III

EXPERIMENTAL

A. General Techniques

1. Spectroscopy

Nuclear magnetic resonance (nmr) spectroscopy was used for structure elucidation and analysis of product mixtures. Nmr spectra were recorded on a Varian A-60 or HA-100 spectrometer. Samples were run in carbon tetrachloride using tetramethylsilane as an internal standard unless otherwise stated.

Infrared (ir) spectroscopy was used in the characterization of compounds. Ir spectra of samples in carbon tetrachloride were recorded on a Perkin-Elmer IR-5A spectrophotometer.

Ultraviolet (uv) spectroscopy was used in the characterization of compounds and as a monitor in the determination of the kinetic parameters of Compound CCCXXV (p 109). Uv spectra of samples in cyclohexane were recorded on a Cary 14 spectrophotometer unless otherwise indicated.

Mass spectroscopy was used to verify structure and to determine isotopic purity of deuterium labeled compounds. Mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6E spectrometer.

2. Flow Pyrolysis

Flow pyrolyses were carried out using a flow-type pyrolysis apparatus consisting of a 3x35cm vertical glass column having a 30cm

hot zone packed with glass beads followed by a series of three Dry Ice-acetone traps. External heating was applied by heating tape and the internal temperature monitored by a thermocouple. Hexane solutions of the sample to be pyrolyzed were injected through a rubber septum at the top of the column while the apparatus was continously flushed with dry nitrogen. Residence time was estimated to be less than one second.

3. Miscellaneous Procedures

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tn.

B. Preparation of Compounds

1. Phenalenone (CCCXXXV)

A modification of the procedure of Lewis and Topsom[119] was used to prepare phenalenone.

To a rapidly stirred suspension of 42.1 g (1 mol, 57% oil dispersion) of sodium hydride in 3 l of anhydrous ether under dry nitrogen, a solution of 170.2 g (1 mol) of methyl-1-naphthyl ketone and 148.2 g (2 mol) of ethyl formate in 500 ml of anhydrous ether was added dropwise. The resulting mixture was refluxed for 18 hours, cooled, and the precipitated sodium salt removed by suction filtration. The salt was washed with anhydrous ether until the washings were colorless. The salt was dried in vacuo and afforded 231.8 g of material contaminated with starting materials.

The dry salt (half-quantity) was slurried in 2 l of chloroform and cooled in an ice bath. The slurried salt was stirred vigorously and 800 ml of 82% sulfuric acid was added dropwise. The resulting mixture was carefully poured into 9 l of water and shaken vigorously. The organic layer was separated and washed once with 2% sodium hydroxide twice with water and then dried over $MgSO_4$. This procedure was repeated with the remainder of the salt and the dried chloroform layers were combined and the solvent removed giving semicrystalline phenalenone which was distilled under vacuum, bp 185-200° (1.0 mm). The product was recrystallized from chloroform-cyclohexane yielding 99.6 g (69.2%) of CCCXXXV (p 113); mp 156.0-156.5° (lit.[120] 156-156.5°). It should be noted that the methyl-1-naphthyl ketone used contained 80% of the 1-isomer and the yield is calculated on this basis.

2. Phenalene (CCCXLVI)

A porous paper thimble containing 12.25g (0.07379 mol) of CCCXXXV (p 113) was placed in a Soxhlet extractor over a 2 l flask and the apparatus flushed with dry nitrogen for 15 minutes. When the system had been thoroughly flushed, 1 l of anhydrous ether, 3.25 g (0.0244 mol) of fresh aluminum chloride and 3.25 g (0.0856 mol) of lithium aluminum hydride were added to the flask. The solution was refluxed until the characteristic yellow color of CCCXXXV (p 113) was no longer visible in the extractor solution. The reaction mixture was allowed to cool and 500 ml of water was carefully added which was followed by 500 ml of 5% hydrochloric acid. The organic layer was separated, dried ($MgSO_4$) and the solvent removed in vacuo.

The product mixture was placed on an alumina column (3x20 cm) and eluted with ligroine collected in 500 ml fractions. Fractions 1-4 contained crude CCCXLVI (p 114) which was recrystallized from ligroine giving 5.30g (64.7%) of white plates of CCCXLVI (p 114): mp 85-86° (lit.[105] 85°).

3. Naphtho [1,' 8'] tricyclo [4.0.0] hept-2-ene, Knoxvalene, CCCXLVIII

Phenalene, CCCXLVI (p 114), 12.20g (0.0734 mol), was dissolved in 1500 ml of anhydrous ether under dry nitrogen with rapid stirring. To this solution, 60.0 ml of 1.5N (0.090 mol) of n-butyl lithium was added dropwise over a 2-hour period. When the addition was complete, the solution was stirred for an additional 1 hour and then cooled to -70°. The temperature was maintained between -65° and -70° while 20 ml of methylene chloride was added over a 1-hour period. This was followed by 80.0 ml of 1.5N (1.20 mol) n-butyl lithium added dropwise over 3 hours. When the n-butyl lithium addition was complete, the reaction mixture was allowed to come to room temperature and stirred for 12 hours. Work-up consisted of adding 400 ml of water and 200 ml of chloroform to the reaction mixture. The mixture was shaken vigorously and the layers separated. The organic layer was dried ($MgSO_4$) and the solvent removed in vacuo giving 16.06 g of dark red oil. The product was shown to be a mixture of CCCXLVIII (p 115) and CCCXXVI (p 109), by nmr. The oil was chromatographed on an alumina column (3x30 cm) which was eluted with ligroine collected in 250-ml fractions. Since the compounds could not be separated by column chromatography, fractions 1-10 were combined giving a yield

of 8.95 g (68.5%) of crystalline product. Nmr analysis showed the product to be composed of 84% of CCCXLVIII (p 115), and 16% of pleiadiene, CCCXXVI (p 109).

In order to separate pleiadiene, CCCXXVI (p 109), from Knoxvalene, CCCXLVIII (p 115), 5.90 g (0.0331 mol) of the above mixture was dissolved in 20 ml of CCl_4 and 6.00 g (0.0345 mol) of diethyl azodicarboxylate was added. The mixture was refluxed for 36 hours under dry nitrogen and the solvent was removed in vacuo. The resulting oil was chromatographed on as alumina column (2x25 cm) which was eluted with ligroine (4 500-ml fractions). Removal of the solvent gave 4.95 g of CCCXLVIII (p 117). Further elution of the column with 50% ether —— 50% ligroine (4 500-ml fractions) gave 1.50 g of the Diels-Alder adduct CCCXXVII (p 109). The CCCXLVIII (p 115) was recrystallized to constant melting point from ligroine giving analytically pure CCCXLVIII (p 115): mp 76.5-77.0°(lit.[107,108] 76.5-77.0); nmr (CCl_4) δ 7.32 (m,6), 3.15 (t,2,J=2Hz), 2.44 (t,2, J=2Hz).

Anal. Calcd. for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.50; H, 5.48.

In an alternate procedure, the mixture of CCCXXV (p 109) and CCCXLVIII (p 115) was recrystallized repeatedly from ligroine until the nmr indicated the presence of only CCCXLVIII (p 115).[108,110]

4. Naphtho [1',8'] bicyclo [3.2.0] hepta-2,6-diene (CCCXXXIV)

A sealed tube containing 4.95g (0.0278 mol) of CCCXLVIII (p 115) in 50 ml of benzene was immersed in an oil bath at 150°

for 12 hours. The tube was cooled, opened and the solvent removed in vacuo. The crystalline product was chromatographed on an alumina column (2x25cm) which was eluted with ligroine collected in 100 ml fractions. Fractions 1 and 2 contained 2.95 g (59.6%) of CCCXXXIV (p 110) which was recrystallized from ligroine and sublimed: mp 118-119° (lit.[96] 118-119°); nmr (CCl_4) δ 7.45 (m,6), 6.36 (s,2), 5.66 (s,2).

Anal. Calcd. for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.58; H, 5.71.

In an alternate procedure, the method of Meinwald and Young was employed[96] with the exception that the oxidation of CCCXXXIII (p 110) with $Pb(OAc)_4$ was carried out in an oxygen atmosphere. The average yield of CCCXXXIV (p 110) obtained in this reaction by this method was 30% in agreement with Nelsen and Gillespie.[95]

The electrolytic conversion of CCCXXXIII (p 110) to CCCXXXIV (p 110) was attempted.[122] A mixture of 2.68 g (0.0110 mole) of CCCXXXIII (p 110), 50 ml of pyridine, 2 ml of water and 250 μl of triethylamine was placed in an electrolysis cell equipped with tin and platinum electrodes. A current of 0.6A and 100V was maintained for 2 hours during which time the reaction mixture required external cooling. Work-up of the reaction mixture revealed no CCCXXXIV (p 110).

5. Naphtho[1',8'] bicyclo[3.2.0] hept-2-ene (CCCLV)

A solution of 1.70 g (9.54 mmol) of CCCXXXIV (p 110) and 0.050 g of Adam's catalyst in 15 ml of 95% EtOH was subjected to atmospheric hydrogenation for 24 hours. The solution was filtered

through Celite and the solvent removend *in vacuo*. The product was chromatographed on a silica gel column (2x15cm) and eluted with ligroine. Fractions of 100 ml were collected and fractions 1-4 contained 1.34g (77.9%) of CCCLV (p 126). Recrystallization from ethanol and sublimation gave pure CCCLV (p 126): mp 74.5-75.5° (lit.[96] 74.0 - 75.5°); nmr (CCl_4) δ 7.45 (m,6), 4.20 (m,2), 2.70 (m,2), 1.85 (m,2); mass spectrum (10/ev) m/e (rel intensity) 180 (77), 152 (100).

Anal. Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.34; H, 6.76.

6. *Naphtho [1',8'] bicyclo [3.2.0] hept-2-ene-d*$_2$ (CCCLVIII)

A 0.500g (2.81 mmol) sample of CCCXXXIV (p 110) was dissolved in 5.00 ml of CH_3OH in a dry nitrogen atmosphere. To this stirred solution was added 1.086 g (5.59 mmol) of potassium azodicarboxylate[123] and 0.40 ml (6.9 mmol) of DOAc followed by two 2.00 ml portions of CH_3OD. The mixture was stirred for 30 minutes and then recharged six times at 30 minute intervals with 0.25 ml (4.3 mmol) of DOAc and 0.25 g (5.1 mmol) of potassium azodicarboxylate. The reaction mixture was stirred for 12 hours and the solvent removed *in vacuo*. The product was chromatographed on an alumina column (2x 20cm) which was eluted with ligroine (100 ml fractions) Fractions 1-2 contained no product. Nmr analysis of fraction 3 showed it to contain 0.290g of a mixture consisting of 95% of CCCLVIII (p 135) and 5% of unreacted CCCXXXIV (p 110).

Fraction 4 contained 0.150 g of product consisting of 84% of CCCLVIII (p 135) and 16% of starting material by nmr. Subsequent fractions contained only a small amount of material (0.020 g) consisting of 70% of CCCLVIII (p 135) and 30% of CCCXXXIV (p 110).

Fractions 3 and 4 were rechromatographed on alumina (3x80cm) and 100-ml fractions collected. Fractions 1-12 contained no product and fractions 13-16 contained 0.171 g of pure CCCLVIII (p 135). Subsequent fractions were contaminated with CCCXXXIV (p 110).

Nmr analysis indicated complete deuteration of the double bond: 4.15 (s,2), 1,85 (d,2, $\underline{J}$=4Hz).

Examination of the nmr spectrum of pure CCCLVIII (p 135) revealed that the signal at 2.70δ in the hydrogenated sample had completely disappeared. Since the protons <u>anti</u> to the bridgehead protons are in the shielding cone of the aromatic ring, they should be upfield relative to the <u>syn</u> protons which are relatively unaffected by the ring current. On this basis the deuterium added <u>cis</u> and <u>syn</u> relative to the bridgehead protons.

7. <u>Pleiadiene</u> (<u>CCCXXVI</u>)

A solution of 4.01 g (22.5 mmol) of a mixture of 67% of CCCXLVIII (p 115) and 33% of CCCXXVI (p 109) in 125 ml of ligroine was injected into a preheated (500°) flow pyrolysis apparatus in

25 ml portions at 15 minute intervals. Each injection of sample was followed by an injection of 25 ml of ligroine. When the entire sample had been injected, the apparatus was cooled and washed with ligroine and chloroform. The reaction product was collected from the traps, combined with the washings and the solvent removed. The product was chromatographed on an alumina column (3x30cm) and eluted with ligroine. Fraction size was 500 ml and fractions 3-8 contained 3.32 g (23.8%) of pleiadiene. Recrystallization from hexane followed by sublimation gave pure red needles of: mp 88-89° (lit.[117] 87-90). nmr (CCl_4) δ 7.42 (m,6), 5.88 (m,2), 5.27 (m,2).

Anal. Calcd. for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: c, 94.29; H, 5.67.

Compound CCCXXVI (p 109) was also produced by the method of Meinwald and Young.[96]

8. 1,8-Divinylnaphthalene (CCCLVI)

1,8-Divinylnaphthalene was prepared by the method of Mitchel and Sondheimer;[111] mp 47-48° (lit.[111] 47-47.5°); nmr (CCl_4) δ 7.57 (m,8), 5.38 (m,4).

9. Compound CCCXXVII (p 109)

This compound was obtained from two essentially identical routes. In the first procedure CCCXXVI (p 109) is an impurity in the synthesis of CCCXLVIII (p 115) and is removed as the Diels-Alder adduct, CCCXXVII (p 109), with diethyl azodicarboxylate. This procedure is described in detail on page 167. This adduct is also

obtained directly from pure CCCXXVI (p 109) by the following method. A mixture of 2.80g (15.7 mmols) of pleiadiene and 3.00g (17.2 mmol) of diethyl azodicarboxylate was dissolved in 100 ml of benzene and refluxed for 18 hours under dry N_2. The reaction mixture was cooled and the solvent removed in vacuo. The resulting orange oil was chromatographed on an alumina column (3x30cm) and 250 ml fractions were collected. The column was eluted with 1 l of 4% ether: 96% ligroine, 1 l of 10% ether: 90% ligroine and 2 l of 50% ether: 50% ligroine. Fractions 1-4 contained a small amount of red solid (less than 10mg), fractions 5-8 contained unreacted diethyl azodicarboxylate, and fractions 9-16 contained 3.80 g (68.7%) of CCCXXVII (p 109). A small amount of this glassy material was sublimed for analysis: nmr (CCl_4) δ 7.50 (m,6), 6.46 m(2), 5.94 (m,1), 5.59 (m,1), 4.03 (m,4), 1.06 (m,6); ir (CCl_4) 5.9 μ (C=O).

Anal. Calcd. for $C_{20}H_{20}N_2O_4$: C, 68.16; H, 5.72; N, 7.95. Found: C, 67.91; H, 6.18; N, 7.81.

10. Compound CCCXXVIII (p 109)

To a solution of 1.274 g (0.00362 mole) of CCCXXVII (p 109) in 10 ml of 95% ethanol was added 20 mg of Adam's catalyst. The mixture was then subjected to low pressure hydrogenation for 24 hours. The solution was then filtered through celite and the solvent removed in vacuo. The resulting oil was chromatographed on silica gel (3.30cm) and eluted with 1,125 ml of 10% ether: 90% ligroine followed by 1,125 ml of 50% ether: 50% ligroine. Fractions 6-10 contained 1.115g (85.5%) of CCCXXVIII (p 109) which was a

glassy solid. A small sample was taken for analysis and sublimed twice: ir (CCl_4) 5.9 μ(C=O); nmr (CCl_4) δ 7.53 (m,6), 5.60 (s,1), 5.16 (s,1), 4.00 (m,4), 2.30 (m,4), 1.10 (m,6).

Anal. Calcd. for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N_2, 7.91. Found: C, 67.78; H, 6.25, N, 7.77.

11. Compound CCCXXVIII-d_2 (p 123)

To a solution of 1.527g (4.31 mmol) of CCCXXVII (p 109) in 5.0 ml of CH_3OD under dry N_2, was added 2.97 g (11.2 mmol) of potassium azodicarboxylate[123] and 0.70 ml (4.59 mmol) of DOAc followed by two 2.0 ml portions of CH_3OD. The solution was stirred for 30 minutes and recharged ten times at 30 minute intervals with 0.50 g (2.57) mmol) potassium azodicarboxylate and 0.25 ml (4.2 mmol) of DOAc. The solution was stirred under N_2 for 12 hours and the solvent removed in vacuo. The product was chromatographed on silica gel (2cmx20cm) and eluted with 500 ml of 100% ligroine followed by 1 l of 50% ether: 50% ligroine. Fraction size was 250 ml. Fractions 3-6 contained 1.390g (90.5%) CCCXXVIII-d_2 (p 123). It was not possible to determine the stereochemistry from the nmr: nmr (CCl_4) δ 7.47 (m,6); 5.65 (s,1), 5.16 (s,1), 3.98 (m,2), 2.19 (m,2), 1.02 (m,6).

12. Compound CCCXXV (p 109)

A 0.550g (1.55 mmol) sample of CCCXXVII (p 109) was dissolved in 25 ml of methanol and 5 ml of water and 5.0 g (89 mmol) of potassium hydroxide was added. The mixture was refluxed for 3 hours under nitrogen and then poured into 100 ml of water and extraced with

three 100-ml portions of chloroform. The organic layers were combined, dried ($MgSO_4$) and the solvent removed *in vacuo*. The glassy product was chromatographed on a silica gel column (3x20cm). The column was eluted with 500 ml ligroine followed by 500 ml of 50% ether: 50% ligroine and 100-ml fractions were collected. Fractions 7-9 contained 0.180 g (55.9%) of CCCXXV (p109) which was sublimed giving a glassy solid: uv max (cyclohexane) 4110Å (ϵ 1065) (-N=N-); ir (CCl_4) 5.7 μ (-N=N-); nmr (CCl_4) δ 7.51 (m,6), 6.10 (s,2), 1.98 (d,4,J=2Hz); mass spectrum (5 eV) m/e (rel intensity) 208 (100) 194 (25) 180 (19).

Anal. Calcd. for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.80; H, 5.80; N, 13.33.

13. Compound CCCLIV (p 123)

CCCLIV was prepared in exactly the same manner as CCCXXV (p 109) was prepared from CCCXXVIII (p 109) (see above): nmr 7.46 (m,6), 6.15 (s,2), 2.10 (s,2). Mass spectral analysis (5 eV) showed Compound CCCLIV (p 124) to consist of 73% d_2, 21% d_1 and 6% d_0. The experiments with $Eu(fod)_3d_{30}$ which were used to determine the stereochemistry of the deuterium atoms as *cis* and *syn* have previously been described (p 123).

14. Compound CCCLIII (p 121), Attempted Synthesis

A 1.000 g (2.84 mmol) sample of CCCXXVII (p 109) was dissolved in 10 ml of methanol and 6.0 g (1 mmol) of potassium hydroxide in 20 ml of methanol was added. The mixture was refluxed under dry nitrogen for 16 hours. The reaction mixture was poured

into water and extracted with three 100 ml portions of ether. The ether extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. The product was chromatographed on an alumina column (3x30cm). The column was eluted (100 ml fractions) with 500 ml of ligroine, 500 ml of 50% ether: 50% ligroine and 500 ml of 100% ether. Fractions 3-5 contained less than 10 mg of pleiadiene as the only characterizable product.

15. Compound CCCLIII (p 122), Attempted Synthesis

A 0.100 g (0.561 mmol) sample of pleiadiene, CCCXXVI (p 109), was reluxed with 0.150 g (0.650 mmol) of di-*t*-butyl azodicarboxylate for 18 hours in CCl_4. The solvent was removed *in vacuo* and the nmr of the reaction mixture showed only starting materials. The above procedure was repeated using xylene as the solvent also failed.

A 0.100 g (0.561 mmol) sample of CCCXXVI (p 109) was treated with 0.130 g (0.565 mmol) of di-*t*-butyl azodicarboxylate and 0.2 ml of boron trifluoride diethyl etherate in 100 ml of dry benzene. The reaction mixture was refluxed for 18 hours and poured into ice water. The aqueous mixture was extracted with three 100-ml portions of ether. The ether extracts were combined, washed with 5% $NaHCO_3$, dried ($MgSO_4$) and the solvent removed *in vacuo*. Nmr (CCl_4) analysis of the product showed only unreacted starting materials.

A 0.100 g (0.561 mmol) sample of CCCXXVI (p 109) was treated with 0.130 g (0.565 mmol) of di-*t*-butyl azodicarboxylate and 0.075 g (0.565 mmol) of aluminum chloride in 100 ml of dry benzene. The reaction mixture was refluxed for 18 hours under dry nitrogen.

Work-up and subsequent nmr (CCl_4) indicated that no reaction had occurred.

A 0.100 g (0.0283 mmole) sample of CCCXXVII (p 109) was stirred for 18 hours with 10 mg of potassium in 50 ml of t-butyl alcohol under dry nitrogen. Work-up and subsequent nmr (CCl_4) indicated that no reaction had occurred.

C. Molecular Orbital Calculations

1. Hückel Calculations

Hückel calculations were carried out on 1,8-naphthoquinodimethane, XVII (p 12), to determine the effect of varying β on the sixth and seventh energy levels (E_6 and E_7). The results are presented in Table VII.[124]

2. CNDO and INDO Calculations

In order to carry out CNDO and INDO calculations (p 154) on Compounds CCCLXV (p 138), CCCLXVI (p 138) and CCCLXVII (p 138) it was necessary to obtain the coordinates of each of these molecules. In all three cases a planar naphthalene ring with "real" bond lengths was assumed and the coordinates for this portion of each molecule are identical and are listed only in Table VIII. These coordinates are presented for CCCLXV (p 138), CCCLXVI (p 138) and CCCLXVII (p 138) in Tables IX and X, respectively. The positions of the atoms for all three conformers follow the convention described in the following structure, CCCLXXI.

TABLE VII

VARIATION OF E_6 AND E_7 OF 1,8-NAPHTHOQUINODIMETHANE WITH β

E_6	E_7	β
-0.0000	0.0000	0.00
-0.0033	0.0069	0.01
-0.0067	0.0138	0.02
-0.0100	0.0218	0.03
-0.0133	0.0277	0.04
-0.0167	0.0346	0.05
-0.0200	0.0415	0.06
-0.0233	0.0484	0.07
-0.0260	0.0554	0.08
-0.0300	0.0623	0.09
-0.0333	0.0692	0.10
-0.0366	0.0761	0.11
-0.0399	0.0830	0.12
-0.0432	0.0899	0.13
-0.0465	0.0968	0.14
-0.0498	0.1037	0.15
-0.0531	0.1105	0.16
-0.0564	0.1174	0.17
-0.0596	0.1243	0.18
-0.0629	0.1312	0.19
-0.0662	0.1380	0.20
-0.0694	0.1449	0.21
-0.0727	0.1517	0.22
-0.0759	0.1586	0.23
-0.0792	0.1564	0.24
-0.0824	0.1722	0.25
-0.0856	0.1790	0.26
-0.0888	0.1859	0.27
-0.0920	0.1927	0.28
-0.0952	0.1994	0.29
-0.0984	0.2062	0.30
-0.1015	0.2130	0.31
-0.1047	0.2198	0.32

TABLE VIII

COORDINATES FOR THE TOTALLY PLANAR CASE, COMPOUND CCCLXV (P 138)

Atom	X	Y	Z
C-1	1.24	0.69	0.00
C-2	2.41	0.00	0.00
C-3	2.41	-1.41	0.00
C-4	1.24	-2.10	0.00
C-5	-1.24	-2.10	0.00
C-6	-2.41	-1.41	0.00
C-7	-2.41	0.00	0.00
C-8	-1.24	0.69	0.00
C-9	0.00	0.00	0.00
C-10	0.00	-1.41	0.00
C-11	-1.53	1.95	0.00
C-12	-0.77	3.27	0.00
C-13	0.77	3.27	0.00
C-14	1.53	1.95	0.00
H-1	3.35	0.54	0.00
H-2	3.35	-1.95	0.00
H-3	1.24	-3.18	0.00
H-4	-1.24	-3.18	0.00
H-5	-3.35	-1.95	0.00
H-6	-3.35	0.54	0.00
H-7	-2.61	1.95	0.00
H-8	-0.98	3.86	0.00
H-9	-0.98	3.86	0.00
H-10	0.98	3.86	0.00
H-11	0.98	3.86	0.00
H-12	2.61	1.95	0.00

TABLE IX

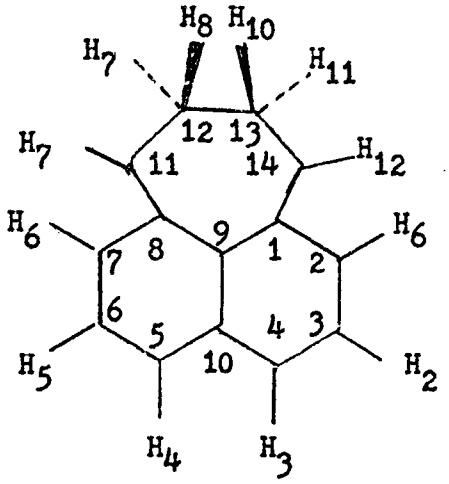
COORDINATES FOR THE SKEWED DIRADICAL, COMPOUND CCCLXVI (P 138)

Atom	X	Y	Z
C-11	-1.24	2.15	0.00
C-12	-0.16	2.91	0.75
C-13	0.16	2.91	-0.75
C-14	1.24	2.15	0.00
H-7	-1.91	2.69	-0.54
H-8	0.14	2.61	1.75
H-9	-0.56	3.91	0.84
H-10	0.56	3.91	-0.84
H-11	-0.14	2.61	-1.75
H-12	1.91	2.69	0.54

TABLE X

COORDINATES FOR THE BENT DIRADICAL, COMPOUND CCCLXVII (P 138)

Atom	X	Y	Z
C-11	-1.24	2.15	0.00
C-12	-0.73	2.91	1.21
C-13	0.73	2.91	1.21
C-14	1.24	2.15	0.00
H-7	-1.56	2.69	-0.88
H-8	1.00	2.43	2.12
H-9	-1.00	3.94	1.17
H-10	1.00	2.43	2.12
H-11	1.00	3.94	1.17
H-12	1.56	2.69	-0.88



CCCLXXI

D. Kinetics

A 16-20 mg sample of Compound CCCXXV (p 109) was placed in a 100-ml volumetric flask and tetrachloroethylene was added to the mark. The solution (3.00 ml) was then pipeted into vials which were degassed by repeated "freeze-pump-thaw" cycles and sealed. The sealed vials were placed in a thermostated bath at the desired temperature. Vials were removed at the required intervals and quenched by plunging then into cold water. The vials were then opened and the rate of disappearence of CCCXXV (p 109) monitored by uv

spectroscopy since the $n \rightarrow \pi^*$ transition of CCCXXV (p 109) occurs at 4110Å, a region where the products of the decomposition CCCLV (p 126) and CCCLVI (p 126) have a very low molar absorptivity of less than 10.

E. Pyrolysis

1. General Procedure

A 30-60 mg sample of CCCXXV (p 109) or CCCLIV (p 123) was placed in an nmr tube and approximately 0.4 ml of the desired solvent was added. If an internal standard was desired, a small amount of TMS was added. In general the sample was then degassed by repeated "freeze-pump-thaw" cycles and the tube ssaled. The nmr spectrum was recorded and the sample was then placed in an oil bath maintained at the desired temperature. The sample was removed at 15-30 minute intervals, if desired, cooled and the nmr recorded in order to monitor the appearance of product and the disappearance of the initial azo compound. At the end of the pyrolysis the tube was cooled and opened. The contents were chromatographed on silica gel (3x20cm) and eluted with 500 ml of ligroine and 500 ml of 50% ligroine; 50% ether. Fractions of 100 ml were collected. Fractions 2-4 contained the reaction products, CCCLV (p 126) and CCCLVI (p 126) and Fractions 7-9 contained any unreacted starting material.

2. Controls

A sample of CCCLVIII (p 135) in tetrachloroethylene was prepared

as described above and placed in an oil bath (134°). The sample was removed after 15 minutes, 30 minutes, 1 hour and 2 hours, cooled, and the nmr recorded. No change in the material could be discerned. It had not undergone stereorandomization nor produced any detectable amount of 1,8-divinylnaphthalene.

A mixture of 53% CCCLV (p 126) and 47% CCCLVI (p 126) in tetrachloroethylene was prepared and pyrolyzed at 134°. The sample was removed after 15 minutes, 30 minutes, 1 hour and 2 hours of pyrolysis, cooled and the nmr recorded. The ratio of CCCLVI (p 126) to CCCLV (p 126) was found to be invariant with time.

Samples of CCCXXV (p 109) in hexafluorobenzene and tetrachlorobenzene were prepared and TMS was added. The samples were degassed, sealed and immersed in an oil bath at 134.0°. The total amount of material was monitored as a function of time and was found to be constant within the limits of integration. Further the ratio of CCCLVI (p 126) to CCLV (p 126) was constant within the limits of integration.

F. Photolysis

1. General Procedure

A 30-60 mg sample of the compound to be photolyzed was placed in an nmr tube and approximately 0.4 ml of solvent added. If an internal standard was desired, a small amount was added. In general, the sample was then degassed by repeated "freeze-pump-thaw" cycles and the tube sealed. The nmr was recorded and the sealed tube was

placed in the well of the photolysis apparatus. The photolysis was started and the sample removed at 15-30 minute intervals to monitor the reaction by nmr. Upon completion of the photolysis, the sample was cooled, opened and chromatographed as described in the above section.

2. Low Temperature Photolysis

The sample to be photolyzed was dissolved in approximately 50 ml of the desired solvent and the solution placed in the cooling jacket of a Hanovia photochemical reactor. The lamp well was cooled with Dry Ice-acetone or liquid nitrogen as necessary. The reactor well was evacuated and the entire assembly was placed in the well of a New England Photochemical Reactor and irradiated. Upon completion of irradiation, the system was allowed to warm to room temperature and worked-up in the usual manner.

3. Controls

A sample of CCCLIX (p 135) in tetrachloroethylene was prepared and irradiated with 3500Å light for 2 hours. The sample was removed from the reactor after 15 minutes, 30 minutes, 1 hour and 2 hours irradiation and the nmr recorded. No change could be discerned in the sample.

A mixture of 52% CCCLV (p 126) and 48% CCCLVI (p 126) in degassed tetrachloroethylene with TMS was prepared and irradiated with 3500Å light for a period of 2 hours. The sample was removed after 15 minutes, 30 minutes, 1 hour and 2 hours irradiation and

the nmr recorded. The ratio of CCCLVI (p 126) to CCCLV (p 126) was found to be invariant with time as was the total amount of material within the limits of integration.

4. Trapping Experiments

A 70 mg sample of CCCXXV (p 109) was dissolved in 50 ml of carbon tetrachloride and 1 ml of dimethyl acetylenedicarboxylate was added. The solution was irradiated with 3500Å light for 3 hours. Work-up showed only CCCLV (p 126) and CCCLVI (p 126) in the usual ratio of approximately 7:1 (see Tables IV (p 127) and V (p 130)).

A 65 mg sample of CCCXXV (p 109) was dissolved in 75 ml of carbon tetrachloride and 0.50 ml of diethyl fumarate added. The solution was photolyzed for 3 hours with 3500Å light. Work-up showed only CCCLV (p 126) and CCCLVI (p 126) in the usual ratio.

A 60 mg sample of CCCXXV (p 109) was dissolved in 50 ml of carbon tetrachloride and 100 mg of tetracyanoethylene added. The solution was irradiated for 5 hours with 3500Å light. An intractable charge-transfer complex was the only product obtained.

G. Product Identification

The hydrocarbon products, CCCLV (p 126) and CCCLVI (p 126), from several photochemical and pyrolytic decompositions of Compound CCCXXV (p 109) were combined giving 190 mg of material which was placed on an 5% silver nitrate — silica gel column (2x30cm). The column was eluted with 1 l of ligroine and 1 l of 10% ether — 90% ligroine and 100 ml fractions were collected. Fractions 1-5

contained 150 mg of Compound CCCLV (p 126) which was crystallized from methanol and compared with authentic material (p 168). Nmr spectra, melting point and undepressed mixed melting point showed the isolated material to be CCCLV (p 126). Fractions 13-17 contained 30 mg of Compound CCCXXVI (p 109) which was compared with authentic material.[124] Nmr, melting point, and undepressed mixed melting point showed the isolated material to be CCCLVI (p 126).

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