To the Graduate Council:

I am submitting herewith a dissertation written by Michael Neal Burnett entitled "Chemical and Spectroscopic Studies of Three 1,8-Naphthoquinodimethanes." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Richard M. Pagni

Richard M. Pagni, Major Professor

We have read this dissertation
and recommend its acceptance:

Linda J. Magid

Jeffrey M Becker

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Accepted for the Council;

L Evans Post

Vice Chancellor
Graduate Studies and Research

CHEMICAL AND SPECTROSCOPIC STUDIES OF THREE 1,8-NAPHTHOQUINODIMETHANES

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Michael Neal Burnett

August 1979

DEDICATION

The author wishes to dedicate this work to his mother and to the memory of his late father.

ACKNOWLEDGMENTS

The author wishes to express his most sincere appreciation to Dr. Richard M. Pagni for his encouragement, understanding, guidance, and patience throughout the course of this research. Special thanks are extended to Dr. J. Wirz without whose assistance much of this work would not have been possible.

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The author wishes to thank Dr. J. R. Dodd for his esr measurements and Dr. J. Q. Chambers for the use of his esr spectrometer.

ABSTRACT

The chemistry and spectroscopy of three 1,8-naphthoquinodimethanes were investigated. The precursor to the parent system, 1,4-dihydronaphtho[1,8-de][1,2]diazepine, is prepared in several steps from 1,8-bis(hydroxymethyl)naphthalene. Photolytic n,π^* excitation of the cis azo compound causes isomerization to the highly strained trans compound, which rapidly undergoes acid-catalyzed tautomerization to 1,2-dihydronaphtho[1,8-de][1,2]diazepine. Photolytic π,π^* excitation of the azo compound causes nitrogen elimination, giving acenaphthene. The triplet state of the parent 1,8-naphthoquinodimethane was observed via its esr spectrum when the azo compound was photolyzed in a hexafluorobenzene matrix at 77 K. A Curie law study conducted below 20 K showed this triplet state to be a thermally accessible excited state, but later work showed this finding to be in error; the triplet state is the ground state of the molecule. Attempts to trap the quinodimethane with oxygen during the photodecomposition of the azo compound were unsuccessful, but some species present during the photolysis reaction was apparently trapped by nitric oxide. In an alternate route into the unbridged 1,8-naphthoquinodimethane system, cis- and trans-1,2-dihydro-1,2-diphenylacenaphthylene were pyrolyzed and found to undergo cis-trans isomerization, but the exact nature of the intermediate in this process is unknown. Photolysis of these hydrocarbons did not cause isomerization.

The precursor to the one-carbon-bridged 1,8-naphthoquinodimethane, 6b,7a-dihydro-7H-cycloprop[a]acenaphthylene, is prepared by

the reaction of copper, iodine, and methylene iodide with acenaphthylene. Previous deuterium labelling studies indicate that this compound thermally undergoes epimerization faster than a [2,3] hydrogen shift, producing 1H-phenalene. Kinetics measurements which assume the 1,8-naphthoquinodimethane to be a common intermediate in the two processes indicate that ring closure of the intermediate occurs 36 ± 19 times fasters than the hydrogen shift. Failure to trap this presumed intermediate with either oxygen or nitric oxide may indicate that it is not in fact present during the thermal reactions of the cyclopropane.

The precursor to the two-carbon-bridged 1,8-naphthoquinodimethane, 1,4-dihydro-1,4-ethanonaphtho[1,8-de][1,2]diazepine, is prepared in three steps from cyclohepta[de]naphthalene. Both photolysis and thermolysis of the azo compound give 6b,7,8,8a-tetrahydrocyclobut[a]acenaphthalene and 1,8-diethenylnaphthalene in an approximate ratio of 7:1 regardless of solvent. Previous deuterium labelling studies show that the quinodimethane is an intermediate in both processes. A new Curie law study of the esr spectrum of this species indicates that it has a triplet ground state, which is further supported by its electronic spectra and molecular orbital calculations. Photolysis of the azo compound in the presence of oxygen gives a combined 73% yield of the two hydrocarbon products in their normal ratio and a 27% yield of an oxygen adduct. Similar thermal decomposition does not give this adduct. Nitric oxide traps the intermediate of both the thermal and photochemical decompositions to some extent. All of these results are explained by spin statistics.

TABLE OF CONTENTS

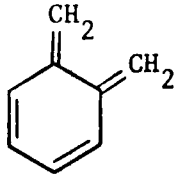
LIST OF FIGURES

CHAPTER I

INTRODUCTION

The subject of this dissertation is the chemical species 1,8-naphthoquinodimethane, one member of the class of organic compounds known as quinodimethanes. In order to understand better the nature of this particular system, a general background to the quinodimethanes will be presented in this chapter. It will include such aspects as molecular orbital calculations, preparations, reactions, and spectral properties of these molecules. This is not intended, however, to provide a complete review of the subject but rather to deal with representative members and characteristics of this class as a whole.

The quinodimethanes may be described as organic quinones in which the two oxygen atoms have been replaced by methylene groups. Most can be represented by simple closed-shell structures, and their spectral and chemical properties show them to be essentially conjugated polyenes. Examples are ortho-xylylene (1) and para-xylylene (2). On the other hand, some members of this class cannot be drawn with a closed-shell structure and may naively be predicted to exhibit the properties of a ground-state triplet biradical. An example of this type is meta-xylylene (3), which corresponds to the hypothetical meta-benzoquinone.



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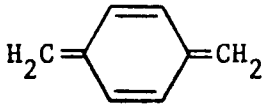

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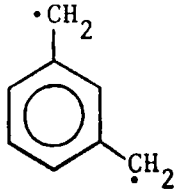


3

A. Molecular Orbital Calculations

The highly conjugated structures of the quinodimethanes made them prime candidates for early molecular orbital calculations, and a number of such studies began to appear in the literature during the 1940's. Employing both the valence bond and Hückel molecular orbital approaches, Namiot, Dyatkina, and Syrkin[1] calculated appreciable resonance energies for the parent xylylenes. The values for the ortho and para isomers are 1.92β and 1.94β, respectively, which are comparable to the 2.0β calculated by the same method for benzene. In addition, m-xylylene was predicted to possess significant stability based on its calculated total π-electron energy of 9.42β, which is only slightly less than that of the ortho (9.92β) and para (9.94β) isomers.

When p-xylylene was first prepared by Szwarc,[2] he claimed appreciable stability for the species if kept at low concentrations in the gas phase. However, failure in later years to isolate and directly observe the simple xylylenes tended to contradict the early predictions of stability (i.e., stability in the sense that the material can be isolated and maintained at room temperature). Thus, more sophisticated calculations were performed on them and the higher quinodimethanes.

One of the most comprehensive studies, including 32 members of this class, was published by Gleicher, Newkirk, and Arnold.[3] The method employed was a variation of the Pople-Pariser-Parr (PPP) approach to self-consistent field (SCF) calculations developed by Dewar and Gleicher.[4] The modification allows variation in the bond lengths

of the molecule during the computation until the total energy of the system is minimized. This approach was found to work remarkably well for planar conjugated systems, giving values for heats of formation and bond lengths very close to those determined experimentally.[4]

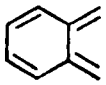
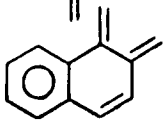
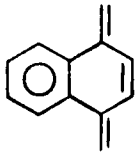
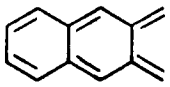
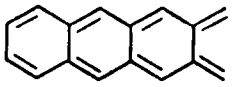
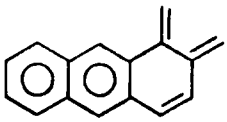
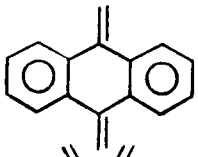
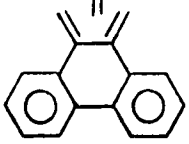
Table I includes the resonance energies of several quinodimethanes calculated by the method of Dewar and Gleicher.[3] In sharp contrast to the early calculations, the new study indicates very low resonance energies for o- and p-xylylene (compare benzene with a resonance energy of 1.318 eV calculated by this method[4]); and, in fact, the calculated value for the para isomer is negative. These results are in keeping with experimental findings that the parent xylylenes can be maintained only under special conditions and that very few stable derivatives are known.

With regard to the higher quinodimethanes, the calculations by Gleicher et al.[3] reflect the same trend as that predicted by simple resonance theory: the resonance energies of those systems for which only a single closed-shell resonance structure can be drawn are found to be far less than those of isomeric systems with several resonance structures. For example, this is shown clearly by the 1,2-, 1,4-, and 2,3-naphthoquinodimethanes (4, 5, and 6, respectively, p 4), of which 6 possesses less than one-fourth the resonance energy of 4 and 5.

Secondly it may be noted that only those quinodimethanes with benzenoid rings present have significant resonance energies. Thus, it appears that the resonance energies of these molecules arise primarily from the benzenoid portion of the molecule while the quinonoid

TABLE I

CALCULATED QUINODIMETHANE RESONANCE ENERGIES

Compound	Number	Resonance Energy (eV)
	1	0.095
	2	-0.023
	4	0.988
	5	0.932
	6	0.219
	7	0.306
	8	1.434
	9	1.851
	10	1.861

portion has highly localized bonds with little aromatic character. This idea is supported by the calculated bond lengths.[3] They indicate alternating single and double bonds in the quinonoid part of the molecule with intermediate length aromatic bonds in the benzenoid part.

The PPP SCF calculations by Gleicher et al.[3] predict a triplet biradical ground state for m-xylylene in agreement with Hückel theory, which indicates triplet ground states for those quinodimethanes that cannot be represented by a simple closed-shell structure.[5] However, these same PPP SCF calculations of the triplet state energies of o-xylylene, p-xylylene, and many of the higher quinodimethanes indicate that their triplet states are also more stable than the singlets. This result finds no support in experiment. Thus it appears that these calculations are deficient in their treatment of the triplet states.

Flynn and Michl[6] have also performed molecular orbital calculations on the parent xylylenes. Their method also employed the PPP approach but unlike that of Gleicher et al.[3] included configuration interaction (CI), which allows mixing of excited states with the ground state. Their results indicate singlet ground states for o- and p-xylylene and a triplet ground state for the meta isomer. In addition, their calculations indicate that although o- and p-xylylene may be best represented by a conjugated polyene structure, there is also a contribution of a biradical structure to the ground state.

This biradical-like nature is also indicated by free valence calculations by Hückel theory.[5] They show that in all quinodimethanes

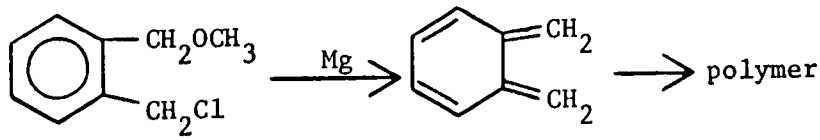
the most reactive sites are the two exocyclic methylene carbons with free valence values comparable to those of organic free radicals. In addition, these same high values are obtained whether the calculation is carried out for the singlet or triplet state. For example, Coulson et al.[7] found free valence values for these positions in p-xylylene of 0.92 in the singlet and 1.13 in the triplet, both of which are comparable to the value of 1.04 for the benzylic carbon in the benzyl radical. Thus, most quinodimethanes should be highly reactive species while the few stable forms should have either special stabilizing groups present or groups that sterically hinder the reactive sites.

B. Ortho Quinodimethanes

Ortho quinodimethanes have been proposed as intermediates in numerous chemical reactions since the 1950's, based not upon their direct observation but rather on reaction products whose structures could most easily be described as trapped forms of the quinodimethane. These highly reactive species are especially susceptible to Diels-Alder reactions due to the formation of aromatic rings in the process. They react with a wide variety of dienophiles, including alkenes, alkynes, and oxygen, as well as the normally less reactive carbonyl, nitrile, and azomethine functions. In the absence of such added dienophiles, the quinodimethanes react rapidly both intermolecularly, resulting in dimers and polymeric material, and intramolecularly, giving cyclobutenes.

o-Xylylene and its derivatives are the most studied members of this class of compounds. Among the earliest works postulating the

intermediacy of o-xylylene (1) is a 1953 paper wherein an attempted synthesis of the Grignard reagent from o-methoxymethylbenzyl chloride (11) failed, and polymeric material with the formula $(C_8H_8)_n$ was produced.[8] Since this work, many examples invoking the o-xylylene intermediate have appeared in the literature, including the examples shown in Equations 2-4.[9]



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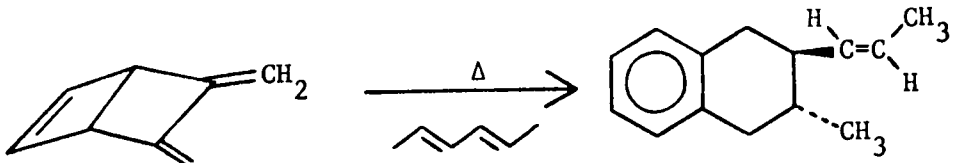

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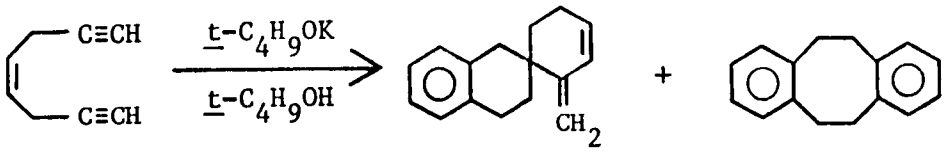

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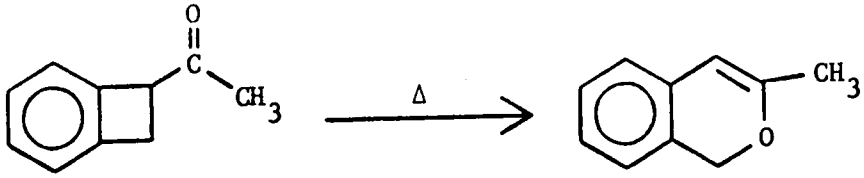
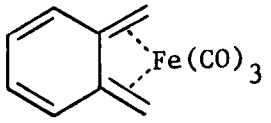


17 18 (4)

Despite the abundance of reactions like these in the chemical literature, direct evidence for the existence of o-xylylenes was difficult to obtain due to their transient lifetimes. In fact, to this time only one simple o-xylylene derivative is known to be stable, the iron complex 19.[10]



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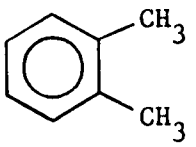
In 1968 Migirdicyan[11] photolyzed o-xylene and 1,2,3-trimethylbenzene at 77 K in a hydrocarbon matrix and obtained the electronic spectra of an entity unknown at that time. The spectra were not similar to any known methyl-substituted benzyl radicals. In addition the spectra were not observed during the photolysis of m-xylene, p-xylene, or toluene, which led Migirdicyan to assign the spectra to o-xylylene.

This assignment was confirmed in 1973 by Flynn and Michl[6] when they recorded the same spectra upon irradiation of each of compounds 20-25 in an ether-isopentane-alcohol (EPA) matrix at 77 K. The



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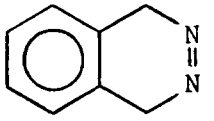

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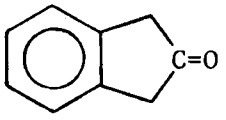

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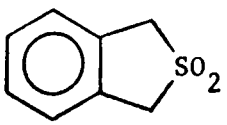

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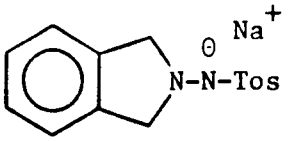

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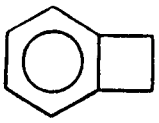
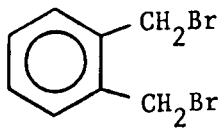


25

observed absorption in the region 24,000-32,000 cm^{-1} matches well the calculated spectrum for transitions between planar S_0 and S_1 states. Also the workers' failure to record an esr spectrum from o-xylylene supports a singlet ground state.

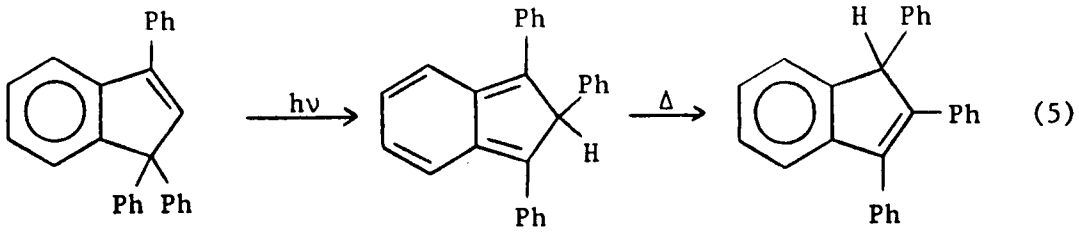
In a later study Tseng and Michl[12] were able to obtain better resolved electronic spectra along with the ir and Raman spectra. They generated o-xylylene in a gas-phase reaction of α,α'-dibromo-o-xylene (26) with sodium or potassium vapor and trapped the intermediate in an argon matrix at 8-30 K.



26

Several cases of stable ortho quinodimethanes are known in which the o-xylylene nucleus is part of a polycyclic system, e.g., isoindenes. Explanations for this thermal stability include--(1) unfavorable geometry for or steric hindrance to dimerization, and (2) the resultant product strain that would result if the compound underwent the preferred conrotatory ring closure to the cyclobutene.

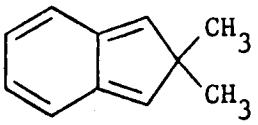
Thus lacking the normal modes of stabilization, the isoindenes are especially prone to [1,5] hydrogen migrations, as illustrated in Equation 5.[13] If, however, groups other than hydrogen are present at



(5)

27 28 29

carbon-2 of the isoindene, the species show considerable stability at room temperature, as is the case in 30[14] and 31.[15] At elevated temperatures, Dolbier et al.[16] have shown that 30 undergoes a concerted [1,5] methyl shift. In the related compound 32, these workers noted that at 190° the ethyl group migrates at a rate seven times that of the methyl group.



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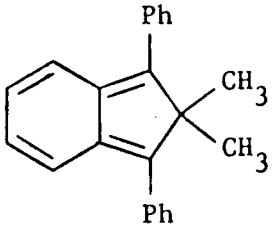

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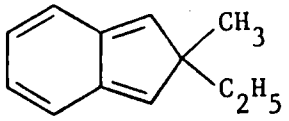
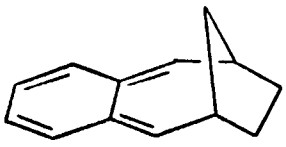


32

The absorption spectrum of 30 is similar to that of o-xylylene but shifted about 2000 cm^{-1} toward longer wavelengths, which is attributed to cyclic hyperconjugation.[14] The nmr spectrum of 30, reported in 1977, was the first obtained for an o-xylylene derivative.[14] Vinyl multiplets at δ 6.08 (4H) and 6.55 (2H) provide evidence for the non-aromatic polyene nature of o-xylylene. Similarly, the chemical shifts of the four protons on the isoindene nucleus in 28 and 31 are δ 6.80 and 6.90, respectively, indicative again of vinyl rather than aromatic protons.[13]

Other polycyclic species reported to possess moderate thermal stability in solution include 33 and 34.[17]



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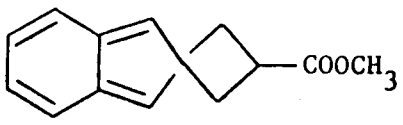

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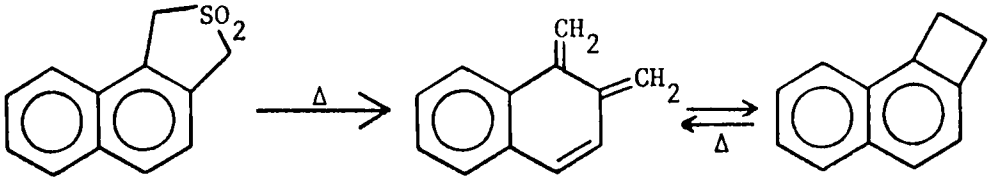
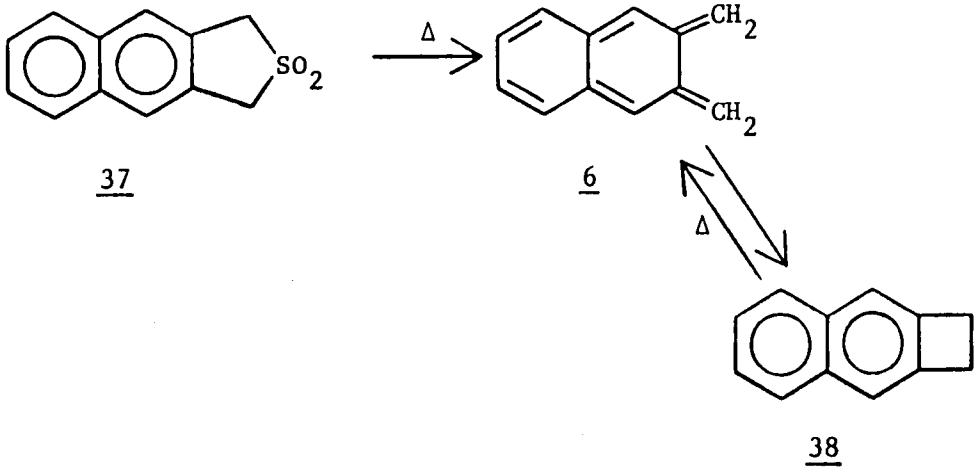
Cava et al.[18] were the first to prepare naphtho[a]cyclobutene (36) and naphtho[b]cyclobutene (38) by thermal decomposition of the corresponding sulfones. Based on the formation of the Diels-Alder adducts when the sulfones were decomposed in the presence of maleic anhydride, the intermediacy of 1,2- and 2,3-naphthoquinodimethane (NQM) (4 and 6) was proposed. Heating the cyclobutenes in the presence of maleic anhydride was found to give again the Diels-Alder adducts. However, at 200° 36 gave its adduct in 53% yield while the adduct of 38 was produced in only 7% yield. From this result, one may infer greater stability of 1,2-NQM over that of 2,3-NQM, in accord with the calculations discussed previously.



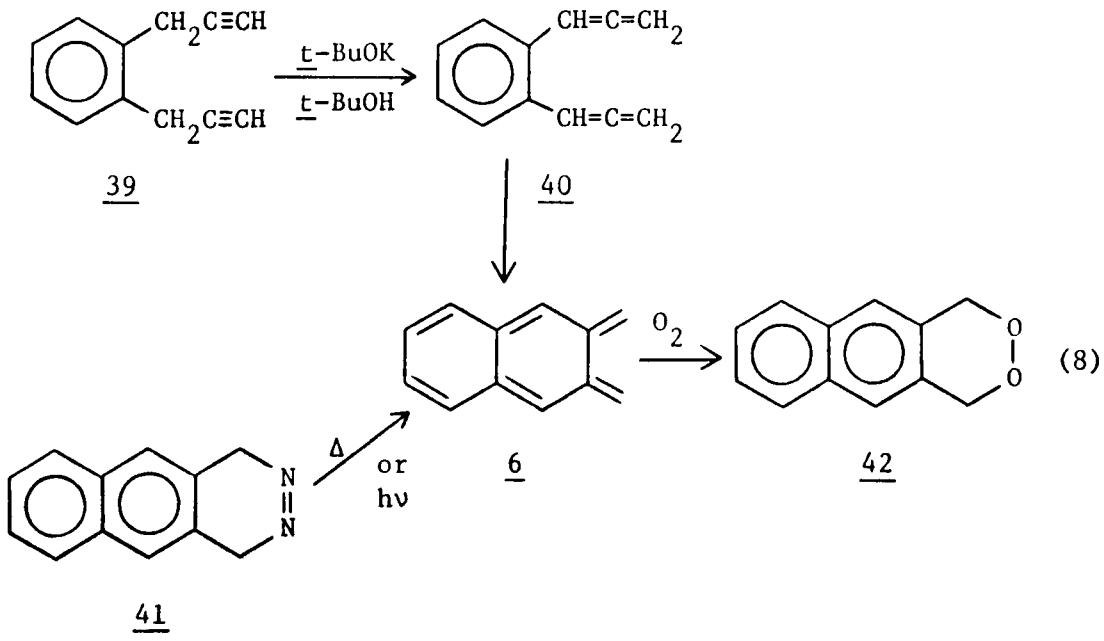
35 4 36 (6)



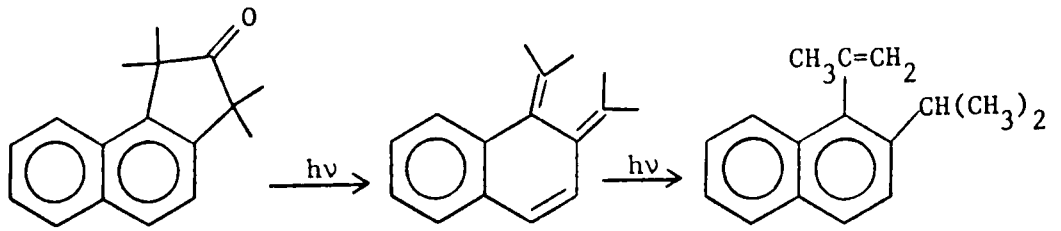
37 6 38 (7)

In addition to the work by Cava's group, 2,3-NQM (6) has been generated from o-dipropargylbenzene (39) and the azo compound 41. Bowes, Montecalvo, and Sondheimer[19] found that treatment of 39 with base led to an intermediate which could be trapped with oxygen to give the peroxide 42. The likely intermediate was 2,3-NQM, being formed from the diallene 40. Careful but rapid workup of the reaction immediately following the addition of the base to 39 allowed isolation of the diallene, but proof for the quinodimethane was not found.

Gisin and Wirz[20] discovered that thermal decomposition of 41 in the presence of air led also to the peroxide 42. When decomposed photolytically at 77 K in a rigid EPA matrix, 41 gave rise to a ruby red material identified via the visible spectrum as 2,3-NQM, which rapidly disappeared upon warming. Whereas o-xylylene absorbed in the region $\bar{\nu} > 24{,}000\ cm^{-1}$,[6] the extended conjugation in 2,3-NQM shifts its electronic absorption to longer wavelengths in the region 16,000-24,000 cm^{-1}.



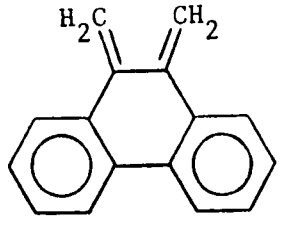
The tetramethyl derivative of 1,2-NQM (44) has been observed during the flash photolysis of the benzindanone 43, as shown in Equation 9.[21] Somewhat surprisingly, 44 was found to be stable indefinitely at room temperature if kept in the dark. The investigators explain this in part by saying that the molecule cannot adopt the planar geometry necessary for the thermally allowed suprafacial [1,5] hydrogen shift. Thus, in the light it undergoes a photochemically allowed antarafacial [1,5] hydrogen shift, producing 45.



(9)

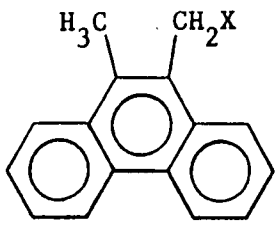
43 44 45

Prior to the direct observation of any o-quinodimethane, Gardner and Sarrafizadeh[22] in 1960 sought to synthesize one member of this class to establish fully their existence. They chose 9,10-phenanthroquinodimethane (10) because the energy difference between this species and the parent hydrocarbon was expected to be small. Attempts



10

to prepare 10 by an elimination reaction from 46 (X = Cl, Br, I) met with failure. However, an apparently successful elimination from 46 ($X = (CH_3)_3N^+ OH^-$) led to the spiro dimer 47 and polymeric material although the intermediate was not observed.



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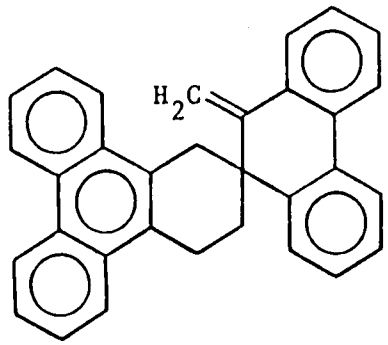
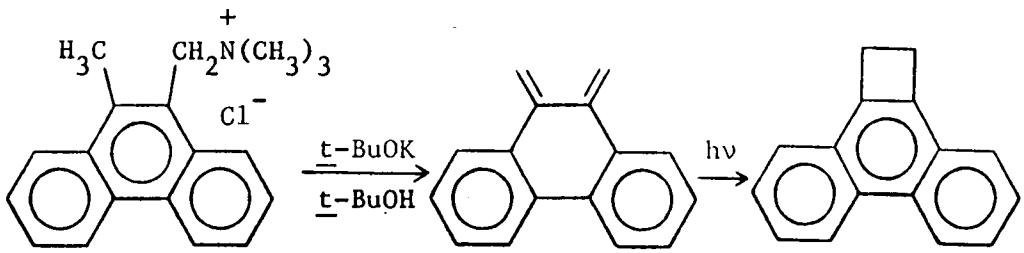


47

Twelve years after this initial work, Anhalt, Friend, and White[23] obtained the ultraviolet spectrum of 10, which indeed was the first direct observation of a simple ortho quinodimethane. Its absorption in the region 33,000-46,000 cm^{-1} is more typical of aromatic species than of conjugated polyenes, which absorb at longer wavelengths. 9,10-Phenanthroquinodimethane (10) was found to exhibit partial stability at room temperature in solution, dimerizing slowly to compound 47. At a concentration of 10^{-3} M in t-butyl alcohol, 10 has a half-life of about 8 hr. Irradiation of 10 produces 49.



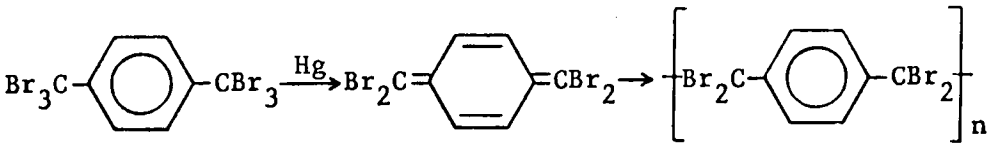
(10)

48 10 49

C. Para Quinodimethanes

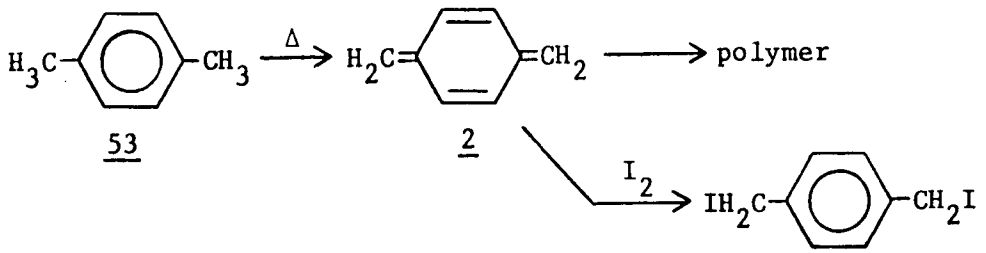
The ortho quinodimethanes have been studied greatly not only because of their theoretical interest but also because of their many synthetic applications, arising primarily from their Diels-Alder reactions. In contrast, the para analogs undergo fewer synthetically useful reactions although they do form numerous polymers with practical utility.

Thiele and Balhorn[24] prepared the first poly-p-xylylene 52 in 1904 by the reaction of mercury with hexabromo-p-xylene (50) and thus likely prepared the first p-xylylene derivative 51. However, a com-



50 51 52 (11)

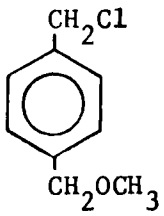
plete study of the para quinodimethanes did not begin until 1947 with the preparation of the parent p-xylylene (2) by Szwarc.[2] He found that pyrolysis of p-xylene (53) led to polymeric material under the same conditions where toluene dimerized to dibenzyl. In addition, introduction of iodine vapor into the pyrolysate gave α,α'-diiodo-p-xylene (54).



53 2 54 (12)

A series of studies on the reactions of p-xylylene began to appear in the chemical literature during the late 1950's. Following the discovery that solutions of this species were stable at low temperature, Errede et al.[25] investigated many of its reactions with a wide variety of organic and inorganic reagents (Figure 1).

In addition to its preparation from p-xylene, p-xylylene has been generated by the reaction of magnesium with 4-methoxymethylbenzyl chloride (55),[26] by a Hofmann elimination reaction of trimethyl-4-methylbenzylammonium hydroxide (56),[27] and by thermal or photochemical cleavage of [2.2]paracyclophane (57).[28]



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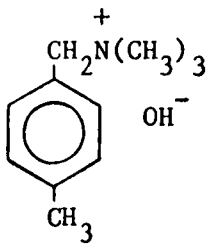

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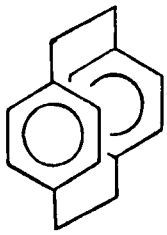
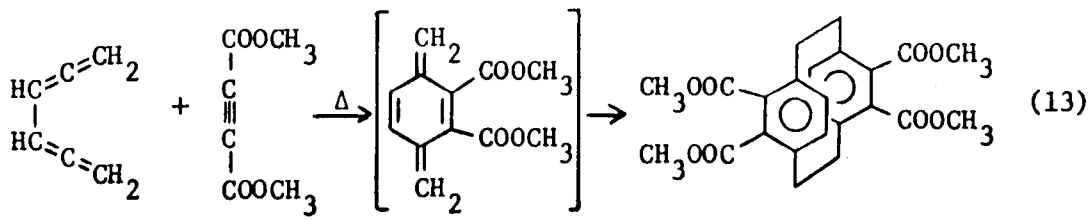


57

A very unusual synthesis from acyclic precursors was published by Hopf[29] following an investigation to determine whether a diallenyl system would undergo [2+2] or [4+2] cycloaddition. Reaction of 1,2,4,5-hexatetraene (58) with dimethyl acetylenedicarboxylate (59) gave in 32% yield the [2.2]paracyclophane 61 possessing the anti configuration. This product arises from dimerization of the substituted p-xylylene 60, the [4+2] cycloadduct.



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58 59 60 61

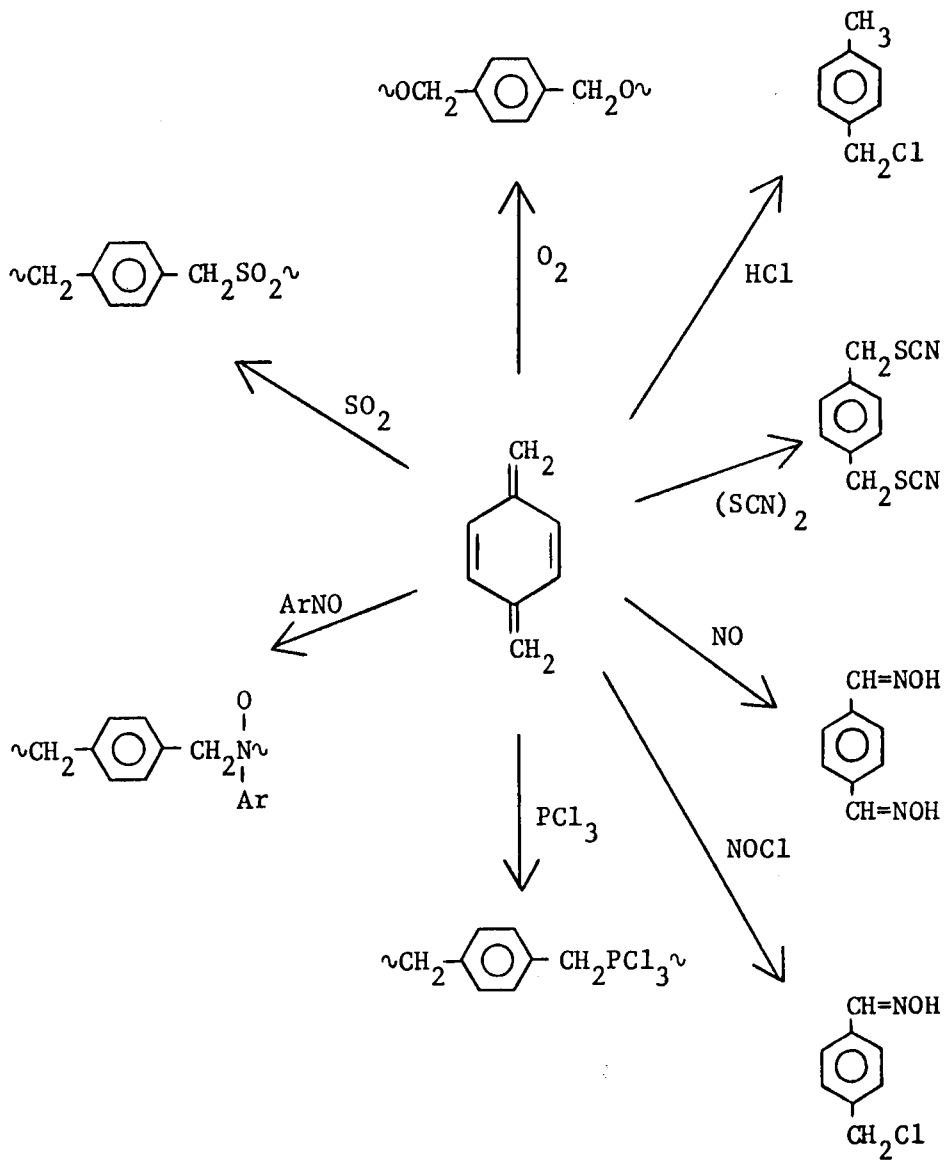
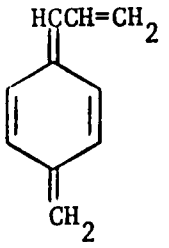


Figure 1. Some reactions of p-xylylene.

Many substituted p-xylylenes have now been prepared, including compounds 62-65, of which 65a-c are stable at room temperature.[30]



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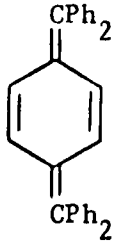

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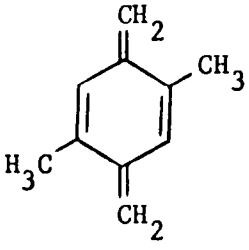
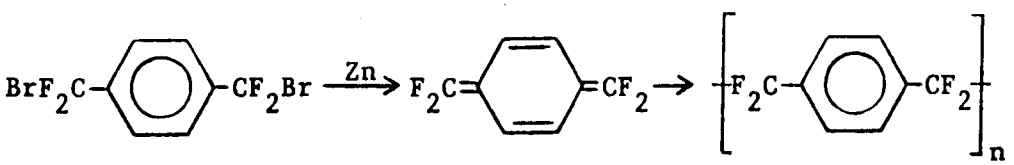


64

65a-c

65a: R = CN
65b: R = $SO_2C_2H_5$
65c: R = CO_2CH_3

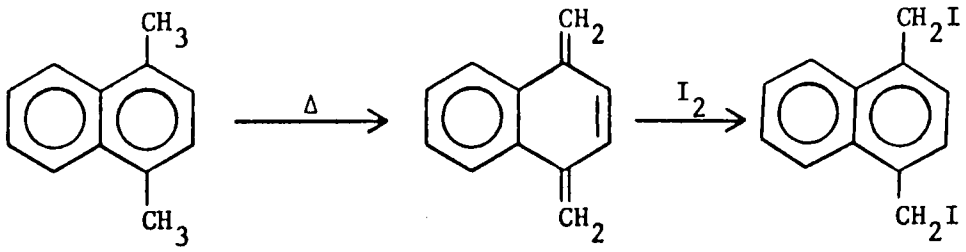
Noting the presence of electron-withdrawing substituents on the stable species, Hertler[31] sought to determine if the stabilization was the result of resonance or inductive effects. He proposed to answer this question by synthesizing the tetrafluoro analog 67, in which the powerful electron withdrawing effects of the fluorines can manifest themselves only by induction, and comparing the stability of this species with that of 65a-c. Heating 66 with zinc gave poly-tetrafluoro-p-xylylene (68), but failure to isolate or detect 67 led Hertler to conclude that the stabilizing effects of the substituents were the result of resonance.



(14)

66 67 68

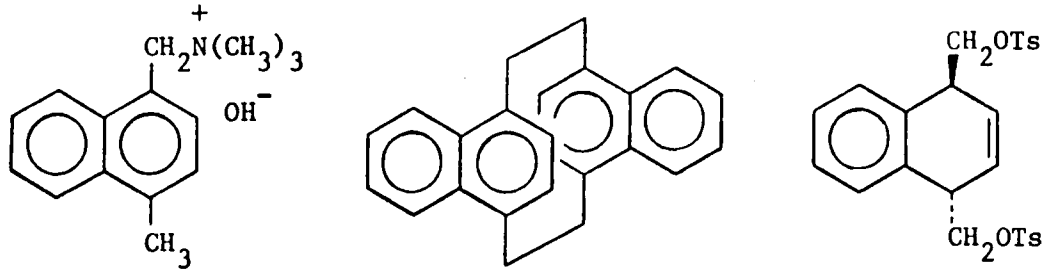
In addition to the parent p-xylylene, Szwarc[32] was the first to prepare 1,4-naphthoquinodimethane (5), again by the pyrolysis of the dimethyl aromatic compound 69. Cram, Dalton, and Knox[33] generated the



(15)

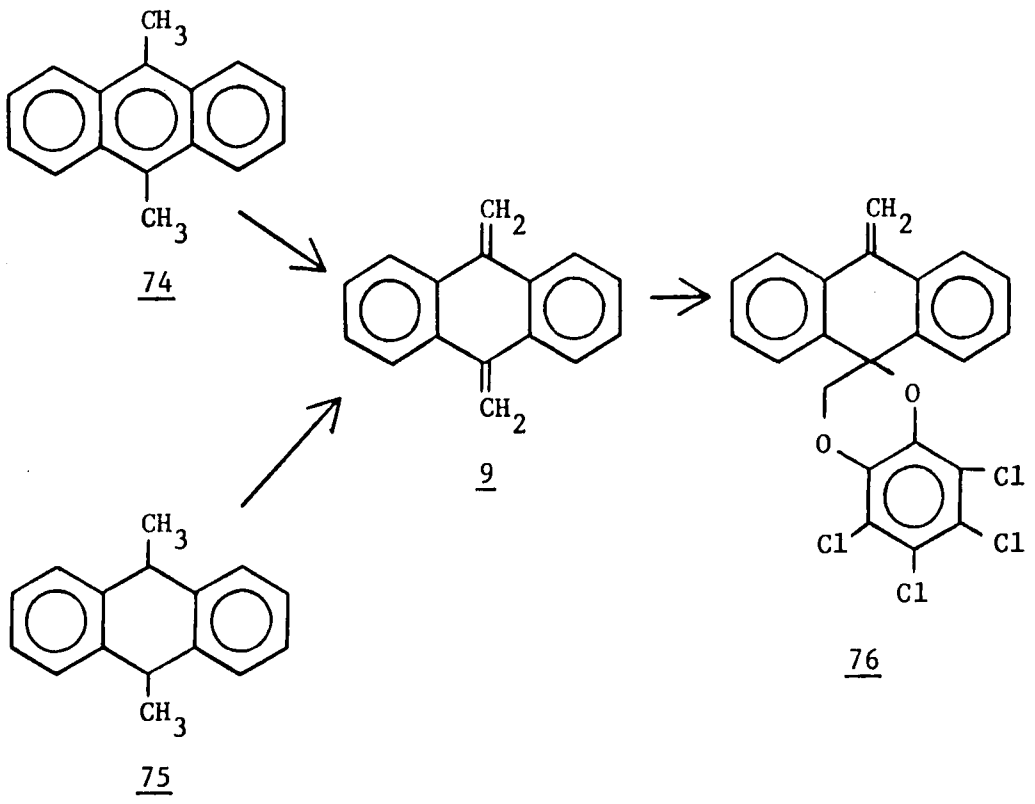
69 5 70

species via a Hofmann elimination reaction of 71 and produced the dimeric cyclophane 72 in the anti configuration in 3.1% yield. Interestingly, Brown and Sondheimer[34] obtained a 90% yield of 72 when the quinodimethane intermediate was generated by heating the ditosylate 73 in pyridine.



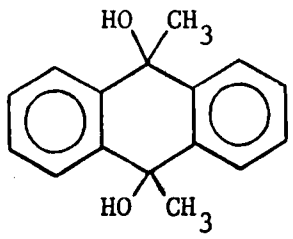
71 72 73

Unlike the pyrolysis of p-xylene and 1,4-dimethylnaphthalene, pyrolysis of 9,10-dimethylanthracene (74) failed to give its corresponding quinodimethane 9. However, Lown and Aidoo[35] found that 74 could be oxidized with chloranil to 9,10-anthraquinodimethane (9) although only the trapped adduct 76 could be isolated. The same reaction could also be performed using 9,10-dihydro-9,10-dimethylanthracene (75) as reactant.



(16)

Millar and Richards[36] generated 9 by thermal dehydration of the cis and trans isomers of 9,10-dihydro-9,10-dimethylanthracene-9,10-diol (77) and discovered that this para quinodimethane reacts with added dienophiles to give the diadduct. For example, 78 is produced from 9 with excess maleic anhydride.



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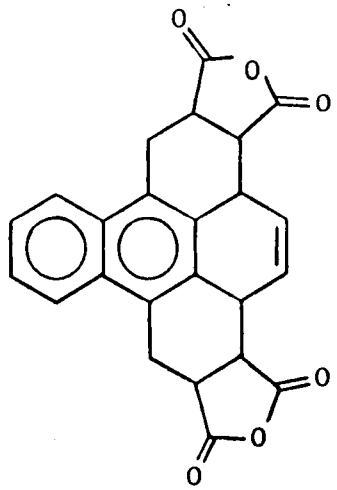
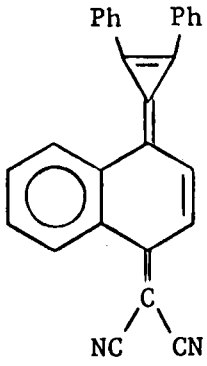


78

Stable forms of both the 1,4-naphtho- and 9,10-anthraquinodimethanes are known in which the methylene carbons bear stabilizing groups, as illustrated by compounds 79 and 80.[37] A second type of stable 9,10-anthraquinodimethane exists in which substituents adjacent to the methylene positions sterically block them from reacting, as in 81 and 82.[38] Bowden and Cameron[39] have studied these systems and have found that even a single methyl group in a peri position will produce a moderately stable species.



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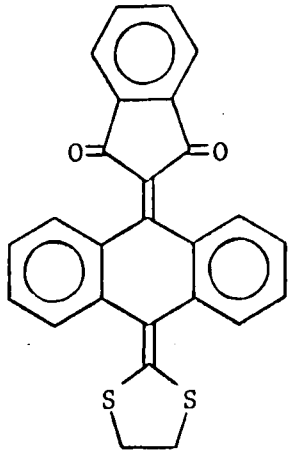

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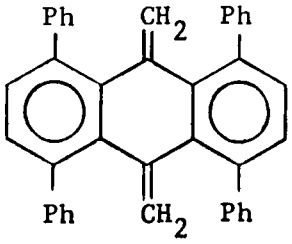

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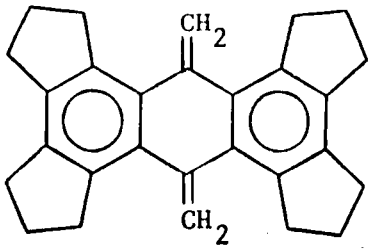
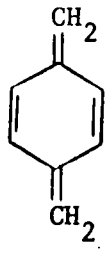


82

Pearson et al.[40] have obtained the nmr spectra of p-xylylene, 1,4-NQM, and 9,10-anthraquinodimethane (2, 5, and 9), which were prepared by pyrolytic cleavage of the corresponding paracyclophanes and trapping of the species at low temperatures. The chemical shifts of the quinonoid ring protons of 2 and 5 are δ 6.49 and 6.61, respectively, indicative of nonaromatic protons. The investigators found that increasing the temperature caused loss of the nmr signal with an accompanying formation of insoluble polymer. In addition, it was noted that as the signal amplitude decreased there was no change in the line widths or chemical shifts. This plus the fact that no esr signals could be observed for these samples indicate singlet ground states and the absence of a triplet biradical in equilibrium with the singlet. Taking the observed rates of disappearance of the nmr signals with increasing temperature as a measure of the relative stabilities of these systems, the order of stability was found to be 9>5>2, in keeping with theory.

Pearson's group[41] also obtained the uv and ir spectra of the three para quinodimethanes in the solid state at 77 K. The uv absorption maxima of the longest wavelength bands are found to be 301, 310, and 295 nm for 2, 5, and 9, respectively. Earlier calculations by



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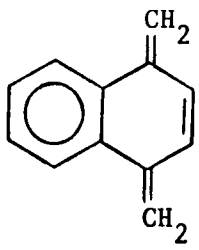

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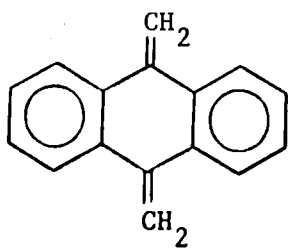


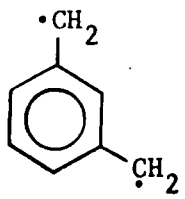
9

Pullman et al.[42] had predicted a hypsochromic shift in these values with maxima of 320, 300, and 275 nm, respectively, which is not reflected by the data.

Koenig et al.[43] have observed the helium(I) photoelectron spectrum of p-xylylene, which is again consistent with the ground state being a singlet polyene. However, based on slightly abnormal bond length values calculated from an electron diffraction study of p-xylylene, Mahaffy, Wieser, and Montgomery[44] note that this species is not "a simple assemblage of conjugated double and single bonds."

D. "Triplet" Quinodimethanes

As mentioned previously, those quinodimethanes for which no closed-shell structure can be drawn are predicted to have triplet ground states.[5] For each of these systems, Hückel theory develops a molecular orbital picture in which the highest occupied energy level consists of a pair of degenerate nonbonding orbitals containing a total of two electrons, resulting in the triplet state. However, the Hückel prediction is derived for these systems from model structures which may not necessarily reflect their true nature. Thus, these species may actually be singlets (hence the quotation marks in the title of this section). Triplet systems that have been investigated include meta-xylylene (3) and 1,8-NQM (83).



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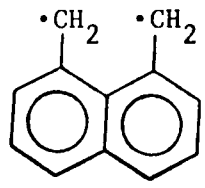
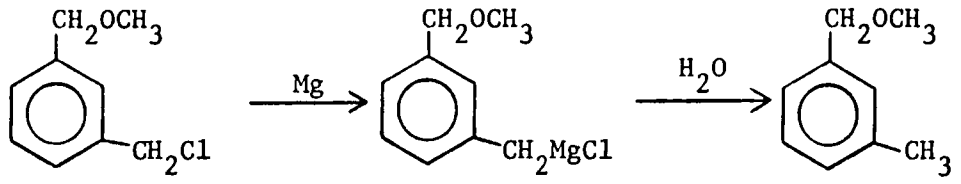


83

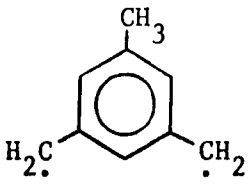
Among the attempts to prepare m-xylylene was that of Mann and Stewart,[8,26] in which they reacted m-methoxymethylbenzyl chloride (84) with magnesium. Whereas elimination reactions had resulted from the ortho and para isomers of 84, the reaction of the meta isomer gave the normal Grignard reagent as shown in Equation 17.



(17)

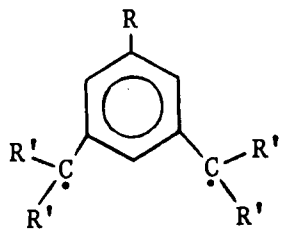
84 85 86

Migirdicyan and Baudet[45] prepared m-xylylene by the photolysis of m-xylene in n-pentane at 77 K, and observed its electronic spectra along with that of 3-methyl-m-xylylene (87). Their calculations show that the ground state of m-xylylene should be the triplet and its first electronic triplet-triplet transition energy should be at 2.90 eV which is in satisfactory agreement with the experimental value of 2.81 eV. The observed similarity of the vibrational fine structure in the fluorescence spectra of m-xylylene with that of the m-xylyl radical indicates that the two species have similar aromatic character. However, an esr spectrum, which could confirm the triplet ground state, was not reported.



87

Schlenk and Brauns[46] first prepared tetraphenyl-m-xylylene (88a)[25] in 1915. In the 1970's Kothe, Denkel, and Sümmermann[47] and Luckhurst, Pedulli, and Tiecco[48] each obtained the esr spectrum of this species. The six-line spectrum is clearly indicative of a triplet biradical, which was shown to be the ground state by a Curie law study. Compounds 88b-d have also been shown to have triplet ground states.[49]



88a-d

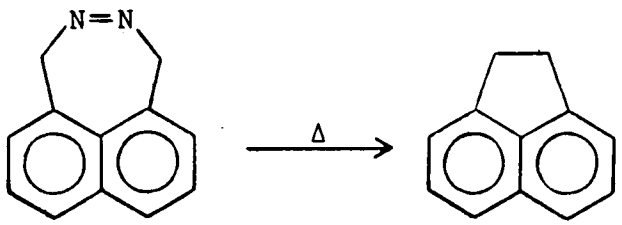
88a: R = H R' = Ph

88b: R = H R' = biphenylyl

88c: R = H R' = terphenylyl

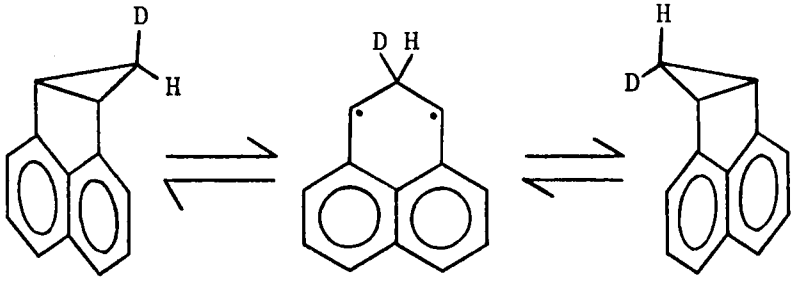
88d: R = Ph R' = Ph

Several reactions have appeared in the literature in which 1,8-NQM (83, p 23) may be an intermediate. For example, Carpino[50] prepared the azo compound 89 and noted that pyrolysis resulted in nitrogen extrusion and the formation of acenaphthene (90). No mention of 1,8-NQM as a possible intermediate in this reaction was made, but Roth and Enderer[51] did postulate its existence to explain the thermal exo-endo isomerization of the deuterated cycloprop[a]acenaphthylene 91, illustrated in Equation 19.



89 90

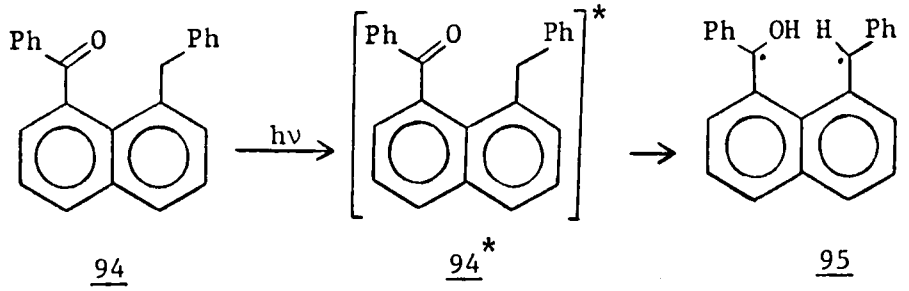
$$+ N_2 \qquad (18)$$



(19)

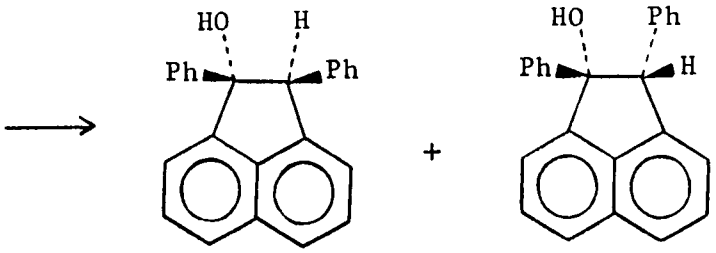
91 92 93

DeBoer et al.[52] published a very detailed study of the photochemical behavior of 1-benzoyl-8-benzylnaphthalene (94), in which they postulated the intermediacy of a 1,8-NQM during the rearrangement. The photoreactive species 94^* was determined to be a π,π^* triplet rather than the more commonly encountered n,π^* excited state of ketones. Hydrogen abstraction by 94^* leads to the 1,8-NQM 95 from which the products 96 and 97 arise.



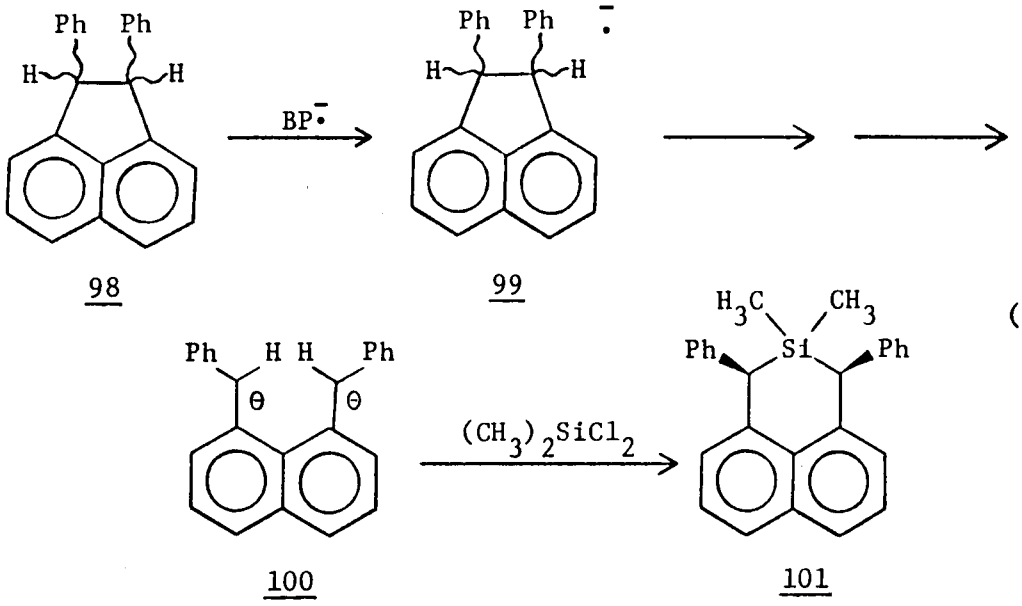
94 94^* 95

(20)



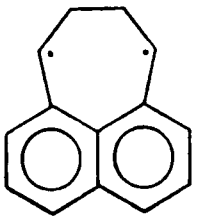
96 97

Bauld and Hudson[53] prepared a stable derivative of 1,8-NQM, namely a dianion. Reduction of either the cis or trans isomer of 1,2-diphenylacenaphthene (98) with the lithium salt of the biphenyl radical anion ($BP^{-\bullet}$) at -78° C gives 99 which upon warming to 0° C opens and apparently undergoes a second reduction to the dianion 100. Trapping of this species with dichlorodimethylsilane gave compound 101 with the phenyl groups cis.



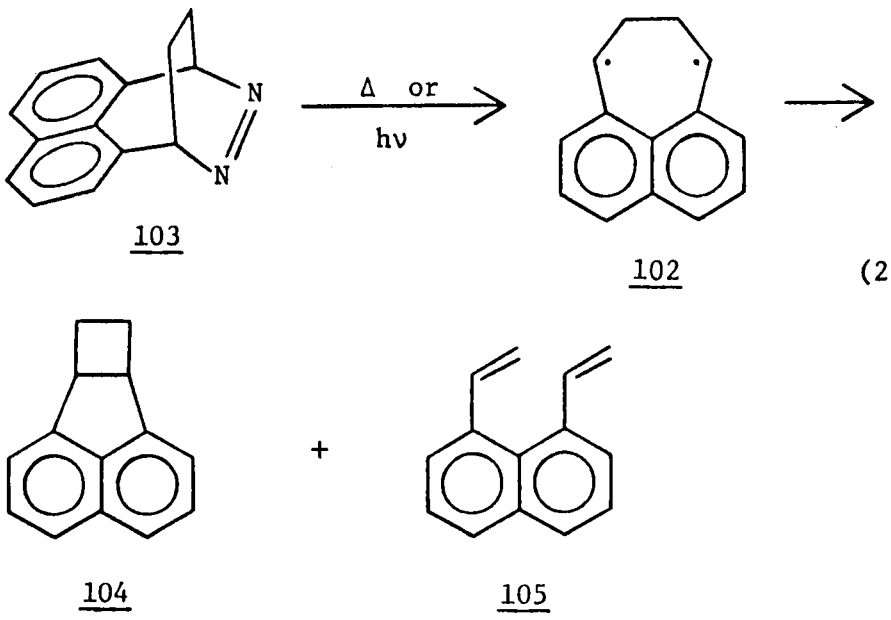
(21)

The first extended study of an uncharged 1,8-NQM came in the work of Watson and Pagni.[54] Rather than the parent compound, however, they investigated the nature and behavior of the two-carbon-bridged species 102.



102

Photochemical or thermal decomposition of the azo compound 103 in a variety of solvents leads to the formation of two products: the cyclobutane 104, the major product, and the divinyl compound 105, the minor. All attempts to trap the presumed intermediate of the reaction met with failure, but decomposition of the azo precursor labelled stereospecifically with deuterium gave products indicating that 102 is indeed an intermediate in the reaction. The esr spectrum of the intermediate clearly showed its triplet state, but a Curie law study indicated that the triplet was an excited state lying 200 cal mol^{-1} above the singlet ground state. Further details of this work will be presented in the next chapter where their discussion is appropriate.



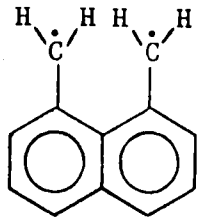
103 → 102 → 104 + 105 (22)

CHAPTER II

RESULTS AND DISCUSSION

A. Background

As stated in the previous chapter, molecular orbital calculations predict a triplet ground state for 1,8-naphthoquinodimethane (83).[5] Figure 2 illustrates the ordering of the Hückel molecular orbitals with their respective energies. Ten of the twelve π electrons of the system are paired in the five bonding molecular orbitals while each of the remaining two electrons is placed in one of the degenerate nonbonding orbitals with their spins unpaired, according to Hund's rule.



83

This picture of a triplet species is based upon a planar model for the 1,8-NQM. However, molecular models indicate that steric interactions between the hydrogens of the methylene groups will force them out of planarity, thereby allowing at least partial overlap of the nonbonding orbitals. As a result of these steric and electronic interactions, the actual bonding scheme may be quite different from that depicted in Figure 2.

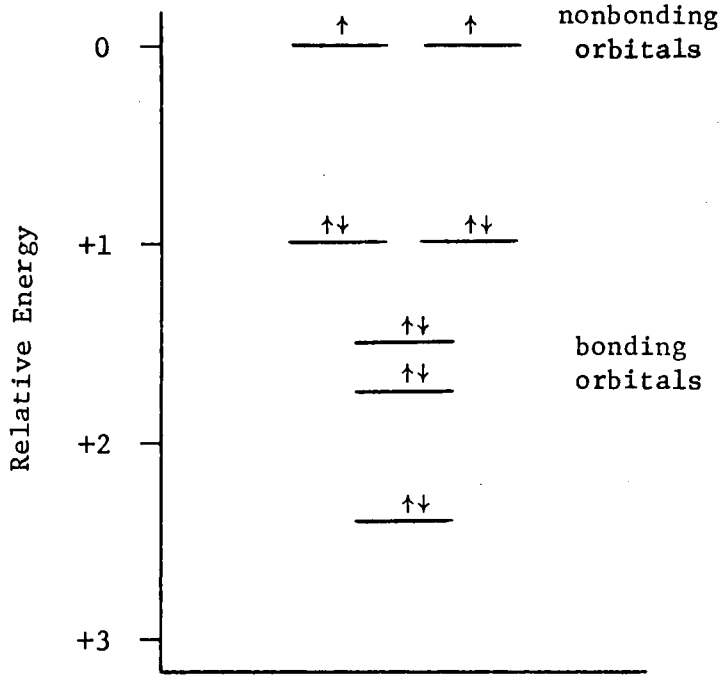
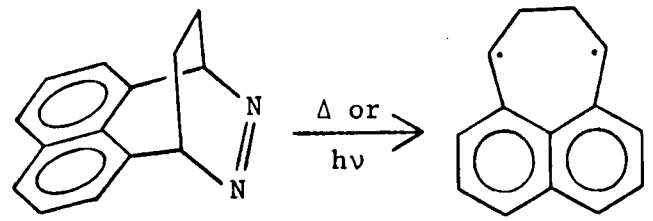
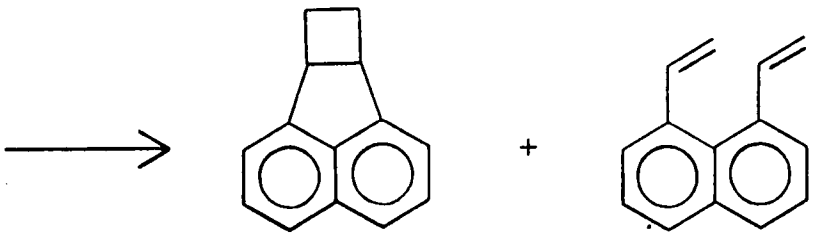


Figure 2. Hückel molecular orbital diagram for 1,8-naphthoquinodimethane.

Watson et al.[54] investigated the nature of the two-carbon-bridged derivative of 1,8-naphthoquinodimethane, (2)1,8-NQM (102). It was generated upon nitrogen elimination from the azo compound 103. Both photochemical and thermal decomposition of 103 led to two products—6b,7,8,8a-tetrahydrocyclobut[a]acenaphthylene (104) and 1,8-diethenylnaphthalene (105) in an approximate ratio of 7:1 regardless of solvent.



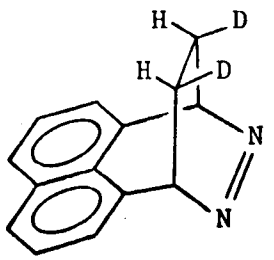
103 102



104 105

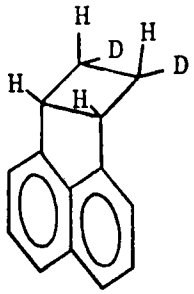
(23)

The proof for the intermediacy of (2)1,8-NQM in the azo decomposition came from an examination of the stereochemistry of the elimination. The dideuterio azo compound 106 was decomposed both thermally and photochemically, again giving only the two hydrocarbons



106

in the same 7:1 ratio. Analysis of the deuterium distribution in these products revealed a 1:1 mixture of the cis,syn (107) and cis,anti (108) isomers of the cyclobutane and a 1:1 mixture of the cis,cis (109) and trans,trans (110) isomers of the divinyl compound. These results are consistent only with the presence of an intermediate with either a planar geometry or equilibrating conformations which average to a planar geometry.



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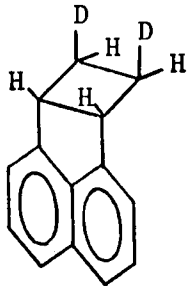

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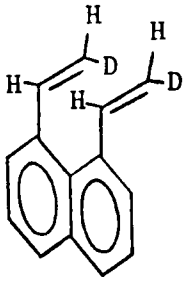

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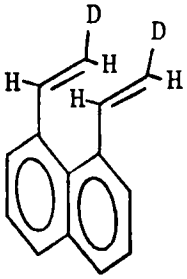
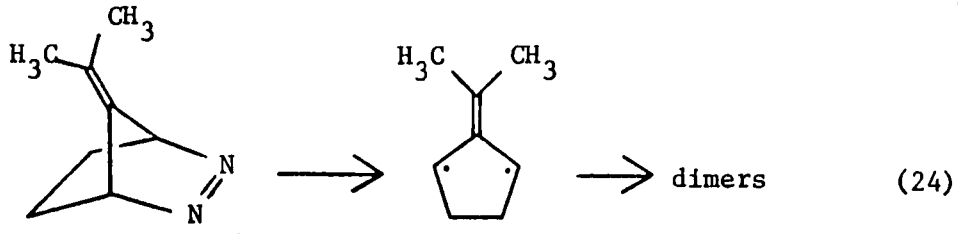


110

The question of the electronic nature of the intermediate remained to be answered. Triplet biradicals are usually longer lived than the related singlet state biradicals and can often be trapped chemically or undergo dimerization. All trapping experiments with a variety of dienophiles failed, and no dimeric products were observed, indicating the intermediate was short lived. Thermolysis and photolysis in several halogenated solvents which should enhance intersystem crossing from an excited singlet state to the expected triplet ground state did not in any way alter the reaction products or their ratio.

Triplet species may sometimes be observed by chemically induced dynamic nuclear polarization (CIDNP), which is the result of spin interactions of two radical centers.[55] CIDNP may be observed as either enhanced absorptions or emission signals in the nmr spectrum of the precursors to and/or the products derived from radical intermediates. In the present case, CIDNP was not observed during either thermal or photochemical decomposition of the azo compound 103 in the probe of an nmr spectrometer.

A closer look at the theory though reveals that CIDNP may not be expected in this case due to the physical proximity of the radical centers in (2)1,8-NQM plus the fact that they are part of the same π system.[55] In the somewhat related triplet biradical system 112, CIDNP is observed in the nmr spectrum of the dimeric reaction products.[56] Most probably the CIDNP arises not as a result of intramolecular interaction between the radical centers but rather from intermolecular interactions between two molecules of 112 as they dimerize.[55] Thus, the lack of CIDNP in the case of (2)1,8-NQM likely reflects only the fact that it does not dimerize.

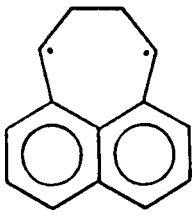


(24)

111 112

The triplet state of (2)1,8-NQM was observed directly by its esr spectrum, obtained at low temperature. A Curie law study indicated that the observed triplet was an excited state lying 200 cal mol^{-1} above a singlet ground state. Although the triplet was observed under conditions where azo decomposition leads to the hydrocarbon products, the extent to which the triplet state plays a role in the reaction could not be determined.

Investigations to be presented in the remaining portion of this dissertation are intended to lead to a better understanding of the 1,8-naphthoquinodimethane system. Further work on (2)1,8-NQM (102) will be included along with new work on the parent system, (0)1,8-NQM (83), and the one-carbon-bridged species, (1)1,8-NQM (113). Much of this work was performed in collaboration with the laboratory of Dr. J. Wirz at the University of Basel in Switzerland. The work of both laboratories will be included here.



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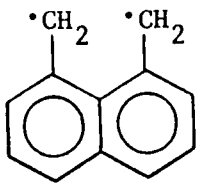

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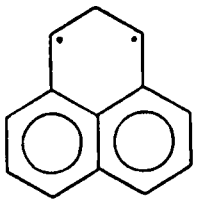
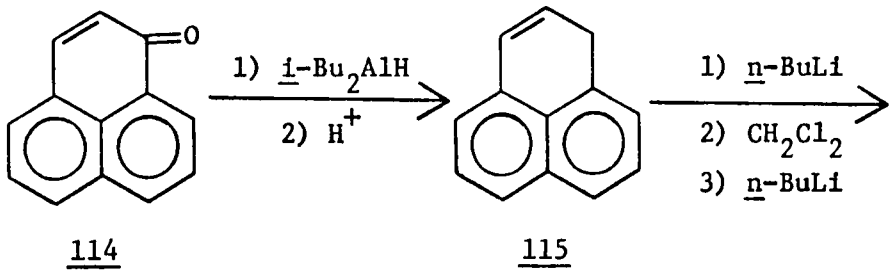


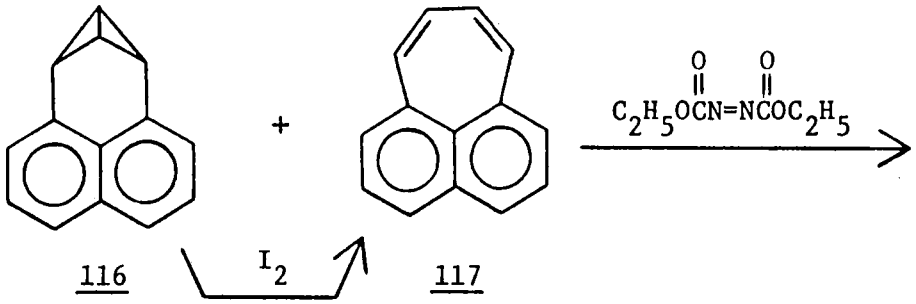
113

B. Syntheses of Precursors

Watson et al.[54] generated (2)1,8-NQM by nitrogen elimination from the azo compound 103. This compound can be prepared by the sequence of steps shown in Equation 25.

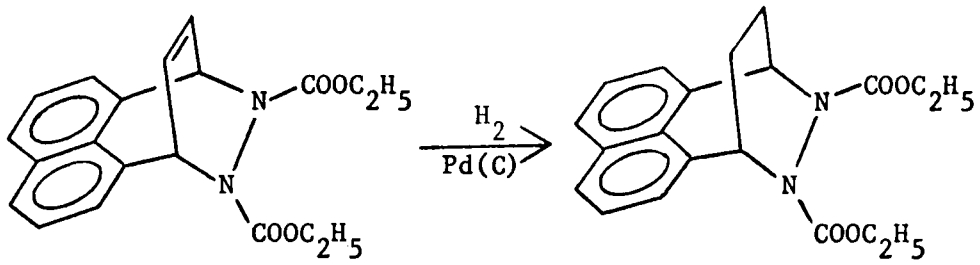


114 115

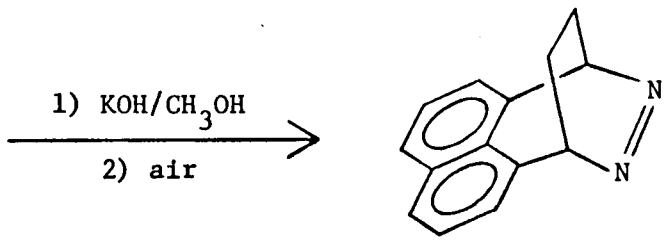


116 117

(25)

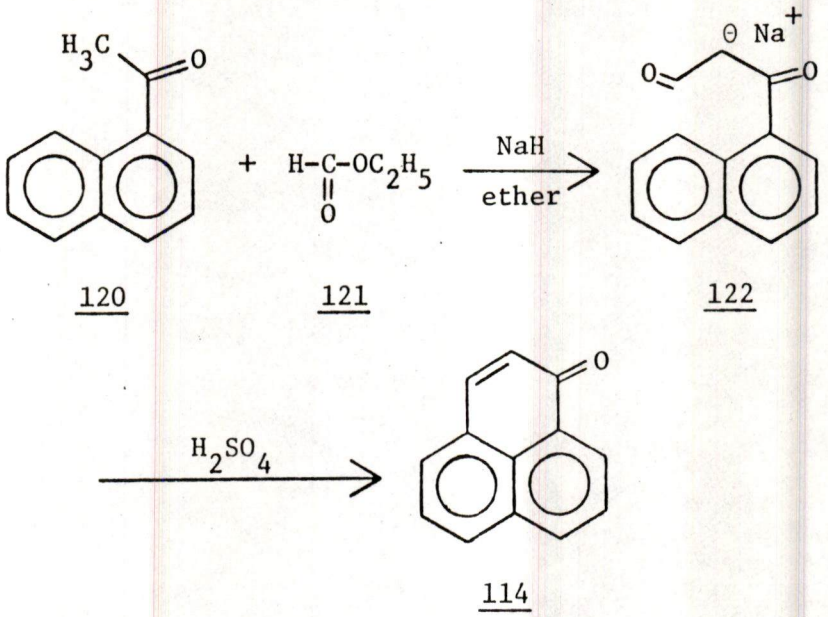


118 119



103

Because of the many steps involved in the preparation of 103, the utility of the sequence shown in Equation 25 depends on the ready availability of large amounts of 1H-phenalen-1-one (114). Watson et al.[54] prepared the material as shown in Equation 26. Their pro-



120 121 122

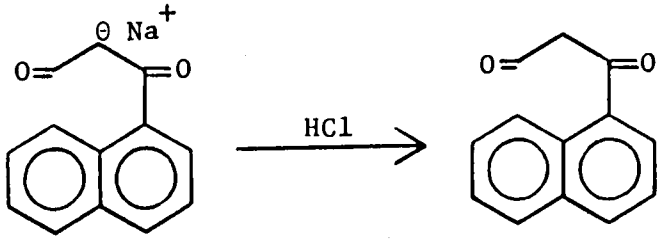
114

(26)

cedure calls for isolating the precipitated intermediate salt 122 by filtration from the reaction mixture and washing with ether to remove unreacted starting materials. After drying, the salt is slurried in chloroform, cooled in an ice bath, and stirred vigorously while 82% sulfuric acid is added dropwise. The product must lastly be purified by vacuum distillation.

This procedure has now been modified in the manner in which the intermediate salt is handled, and several problems associated with the Watson method have been eliminated. First, the precipitated salt is dissolved in water and extracted with ether to remove the unreacted starting materials. This avoids the loss associated with collecting and drying the salt as the solid.

Secondly, the aqueous salt solution is acidified with HCl, causing precipitation of the carbonyl compound 123, which is extracted into carbon tetrachloride. This permits the final ring closure reaction to occur in homogeneous solution rather than with a slurry.

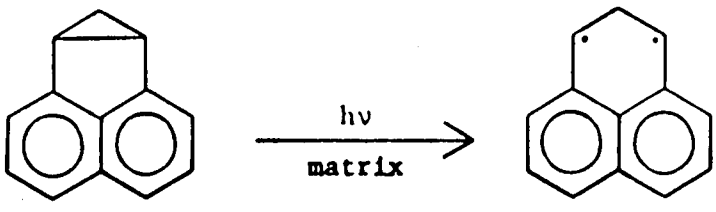


(27)

122 123

Lastly, the solution containing 123 is added to the chilled acid rather than in the reverse manner. The Watson procedure at this last step results in the formation of a black tarry material from which it is difficult to free the phenalenone, necessitating the vacuum distillation. With the reverse addition of 123 rather than the salt to the sulfuric acid, the tarry material does not form, and the product may be purified by simple column chromatography. These modifications increase the yield of phenalenone from 69% (the published yield, but which could not be duplicated) to greater than 90%.

Michl et al.[57] have demonstrated that (1)1,8-NQM can be produced from 6b,7a-dihydro-7H-cyclopropacenaphthylene (124). They prepared

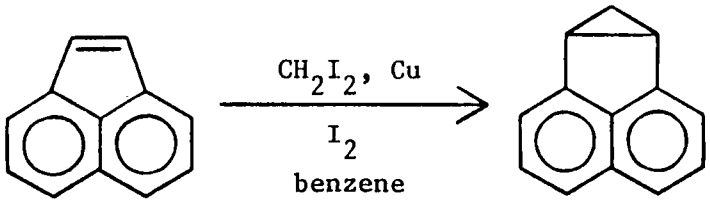


(28)

124 113

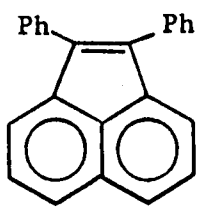
124 by the method of Wittig, Rautenstrauch, and Wingler[58] in which acenaphthylene (125) was reacted with $(ClCH_2)_2Zn$, and 124 is afforded in 49% yield. Because of the difficulties associated with the preparation and handling of this zinc reagent, an easier method of producing the needed carbenoid species was sought. These included the reaction of methylene iodide with a zinc-copper couple,[59] a zinc-silver couple,[60] and with diethylzinc.[61] The first of these failed completely to give any 124 while the zinc-silver couple gave a 30% yield of cyclopropane. Diethylzinc was also found to give a low yield of product, but because of this zinc reagent's high flammability, its use was abandoned.

Finally, the method of Kawabata, Naka, and Yamashita[62] was found to work adequately, and it requires no special handling or preparation of the reagents. As illustrated in Equation 29, refluxing acenaphthylene in benzene with methylene iodide, reagent grade copper dust, and a catalytic amount of iodine produced 124 in 44% yield.

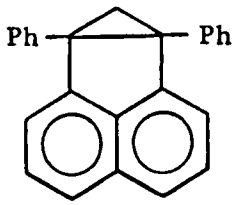


125 124 (29)

An attempt to use this same method to prepare the diphenyl cyclopropane 127 from 1,2-diphenylacenaphthylene (126) was unsuccessful.

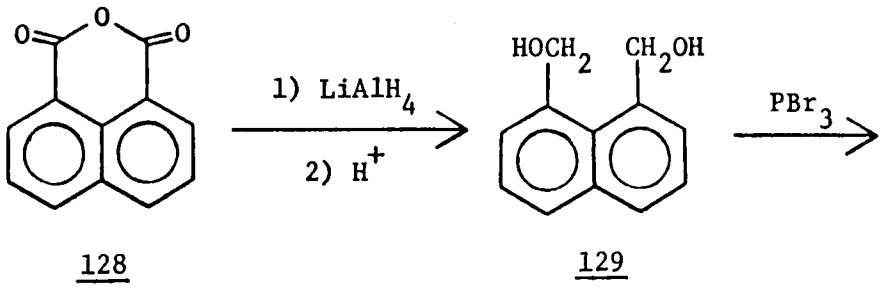


126

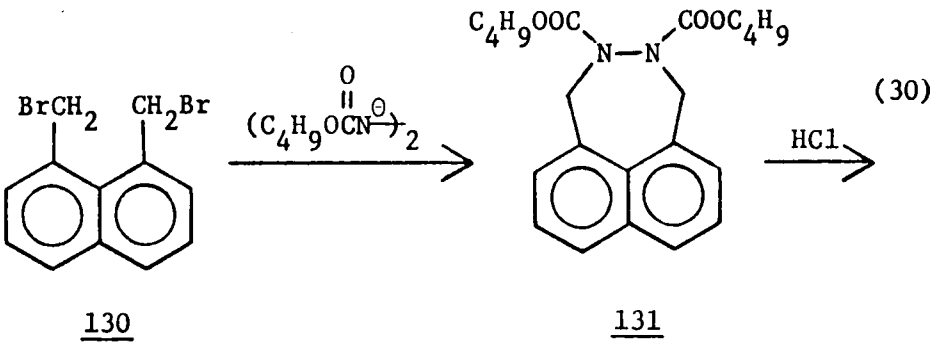


127

A possible route to (0)1,8-NQM is theoretically via nitrogen elimination from the azo compound 89. This material was first prepared by Carpino,[50] and his method of preparation shown in Equation 30 was followed.

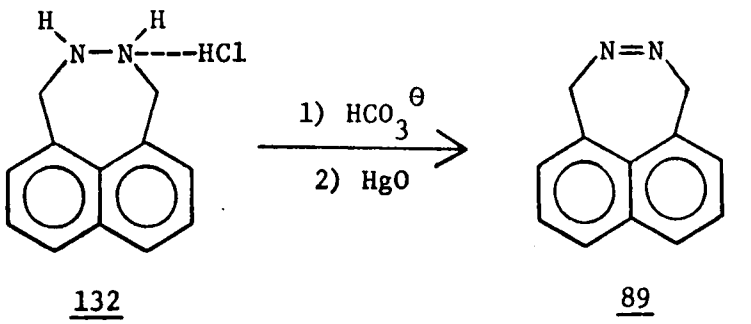


128 129



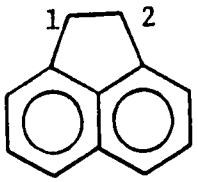
(30)

130 131



132 89

A second potential route into the (0)1,8-NQM system is via cleavage of the C_1-C_2 bond of acenaphthene (90). However, the diphenyl analog 98 was chosen for study as will be described later.



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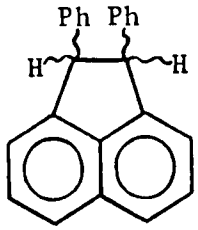
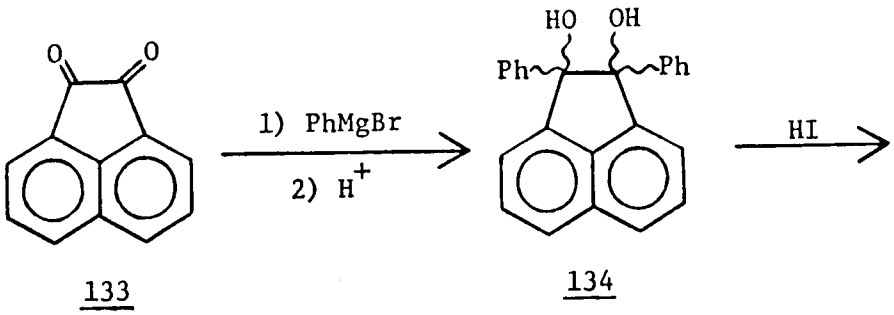
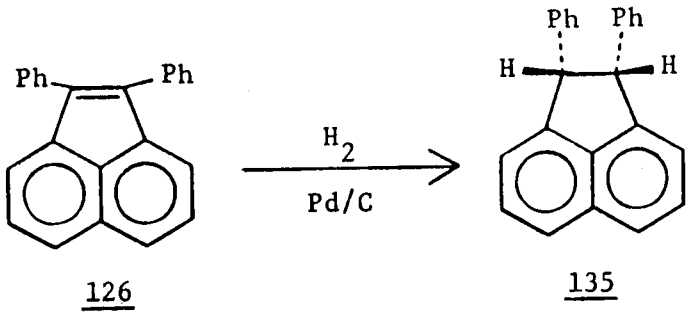


98

The cis (135)[63] and trans (136)[53] isomers were prepared by the sequence shown in Equation 31.

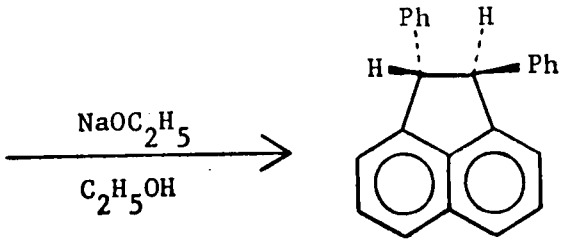


133 134



126 135

(31)



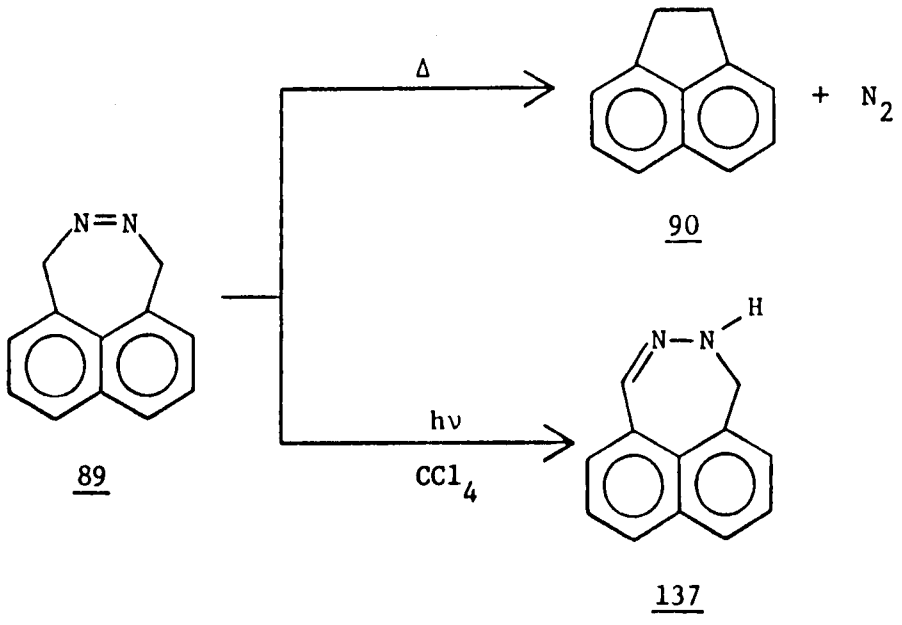
136

C. Attempted Generation of (0)1,8-NQM

1. Nitrogen Elimination from an Azo Precursor

When he first prepared the azo compound 89, Carpino[50] found that its thermolysis led to the formation of acenaphthene (90). Initial attempts in this laboratory to produce the same reaction photochemically met with failure.

Photolysis of 89 in carbon tetrachloride resulted in the sole formation of the tautomeric isomer 137. Carpino[50] had earlier discovered that acid will also cause this transformation. Thus, when it was found that a solution of the azo compound in carbon tetrachloride slowly tautomerizes even in the dark, it was proposed that residual acid in the solvent was largely responsible for the isomerization. However, since the tautomer was produced much more rapidly with photolysis than without, it was clear that light did in some way promote the tautomerization reaction.

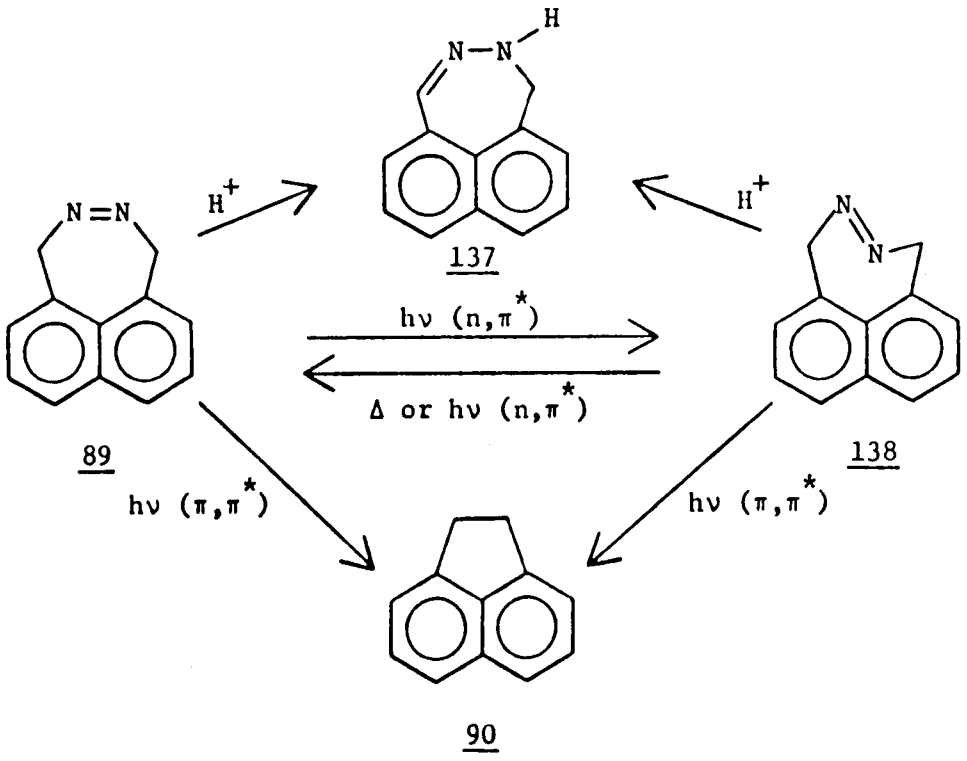


(32)

The azo photolysis was repeated using freshly distilled absolute ethanol for the solvent. Despite this, irradiation of 89 with wavelengths whose energies promote its n,π^* electronic transition (400 nm) again led only to 137. Photoelimination of nitrogen was finally observed when 89 was irradiated with wavelengths whose energies promote its π,π^* electronic transition (315 nm).

When the aprotic solvent benzene was used, only photoelimination occurred with none of the tautomer being observed in spite of the fact that both the n,π^* and π,π^* excited states were being populated. This demonstrates that the tautomerization is indeed an acid-catalyzed reaction rather than a photochemical process.

It was soon discovered that Gisin and Wirz[20] were also investigating this system, and their overall findings are presented in Equation 33.



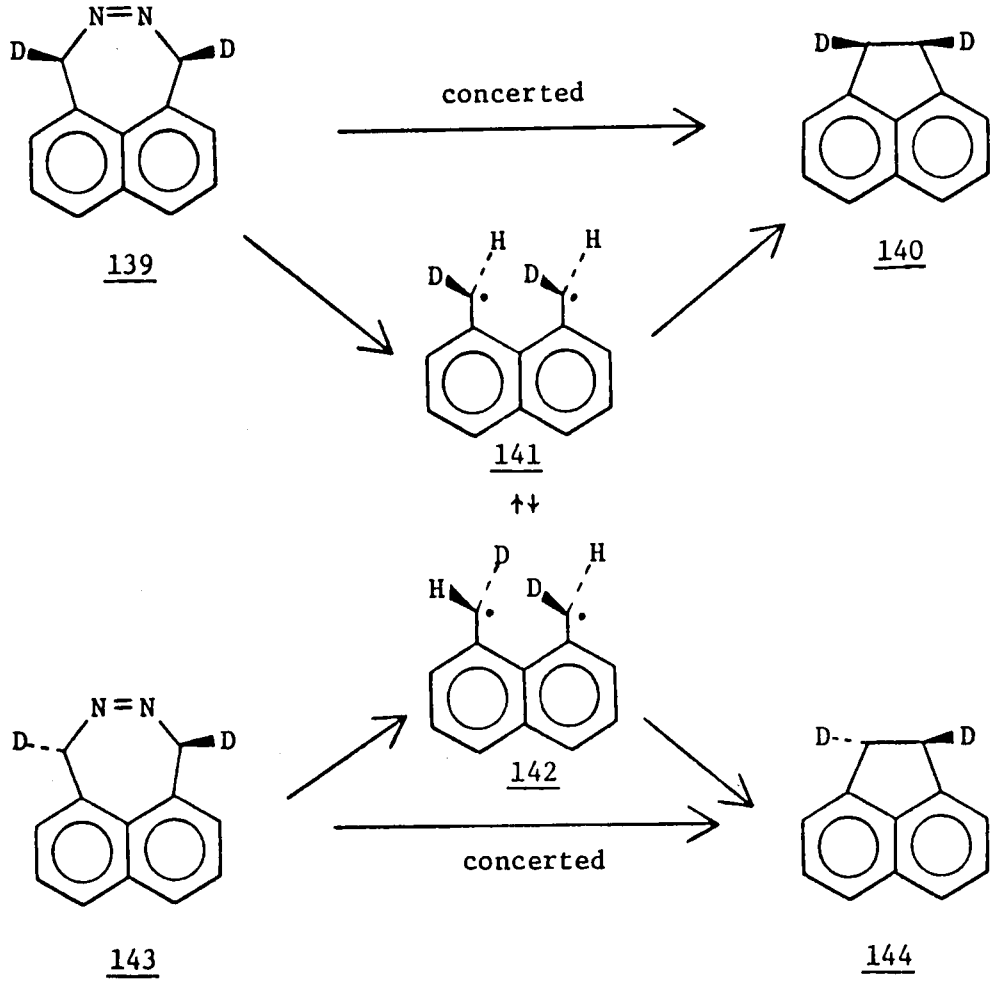
(33)

Irradiation of the azo compound 89 into its n,π^* transition region causes isomerization to the highly strained trans isomer 138, which Gisin and Wirz[20] were able to isolate at low temperature. Acid catalyzes the tautomerization of both azo compounds. However, because of the need to relieve its severe strain energy, the trans isomer is much more vulnerable to acid than its cis counterpart. Thus, acid concentrations too low to promote the isomerization of the cis compound will rapidly tautomerize the trans compound once it is produced photochemically. In the absence of acid, the trans compound will revert either thermally or photochemically (n,π^*) to the more stable cis compound. Lastly, photolysis of either azo isomer into its π,π^* transition region leads to acenaphthene (90).

In spite of the observed formation of acenaphthene from the azo compound, the existence of (0)1,8-NQM as an intermediate in the reaction has not been demonstrated. Gisin and Wirz[20] attempted to verify its presence by direct observation via the absorption spectrum, by chemical trapping, and by flash photolysis of the azo compound, all of which failed. It may be that the intermediate is present in quantities too small to be observed spectroscopically or reacts too rapidly to be trapped. On the other hand, the elimination reaction may be concerted and involve no intermediate at all.

Prior attempts to trap (2)1,8-NQM following the photolysis of its azo precursor had also failed, but its presence was proven by noting the stereochemistry of the elimination.[54] In the present case also, a concerted mechanism should lead to a highly stereospecific reaction while a nonconcerted mechanism involving the quinodimethane

should lead at least to partial loss of stereochemistry in the product. These ideas are illustrated in Equation 34.



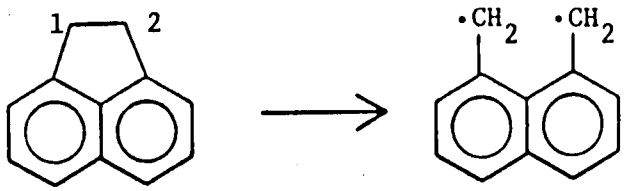
(34)

Although this scheme is theoretically sound, it lacks practical utility because it would be difficult if not impossible to distinguish spectroscopically the cis- and trans-dideuterioacenaphthene products (140 and 144). Because of this, groups other than deuterium would be required to serve as stereochemical markers. However, placing such groups stereospecifically into the starting material would be difficult and was not attempted.

As will be described later, (0)1,8-NQM was observed via its esr spectrum as a product of the azo decomposition. It was found, though, that prolonged irradiation was required to build up the concentration of the species to an observable level. This and other factors lead to the conclusion that the azo decomposition is largely a concerted process with the quinodimethane playing a very minor role in the reaction.

2. Ring Opening of an Acenaphthene Derivative

A second theoretical pathway to (0)1,8-NQM is by homolytic cleavage of the C_1-C_2 bond of acenaphthene (90) although in reality such a process might be expected to require a great deal of energy.

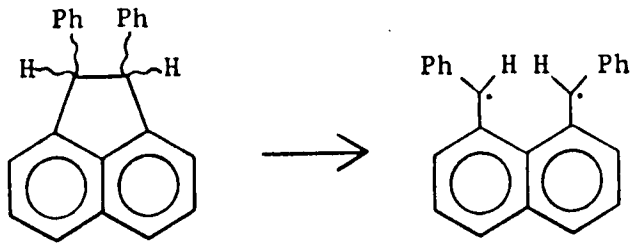


(35)

90 83

It is possible to calculate an approximate enthalpy of reaction for this ring opening from which its feasibility may be estimated. Benson[64] has compiled the heats of formation for a large number of chemical groups. By summing the appropriate values, molecular heats of formation may be found, and from these heats of reaction may be derived. Using Benson's method, ΔH_r° for the reaction in Equation 35 is predicted to be roughly +50 kcal mol^{-1}. Since the reaction is endothermic, the required activation energy will then be at least +50 kcal mol^{-1}, a value indicating little likelihood of its occurring except under the most vigorous of reaction conditions.

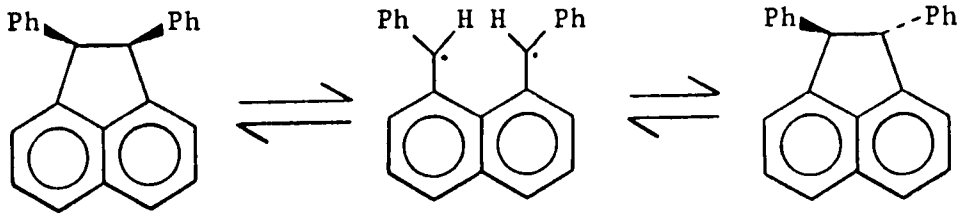
On the other hand, the diphenyl analog 98 might be expected to show a lower reaction enthalpy because the phenyl groups should help to stabilize the radical centers in the quinodimethane. Again using Benson's method,[64] ΔH_r° for the reaction in Equation 36 is found to be ~18 kcal mol^{-1}. This smaller value, although only an estimate, may be taken in support of a greater likelihood that this reaction can be brought about.



(36)

98 145

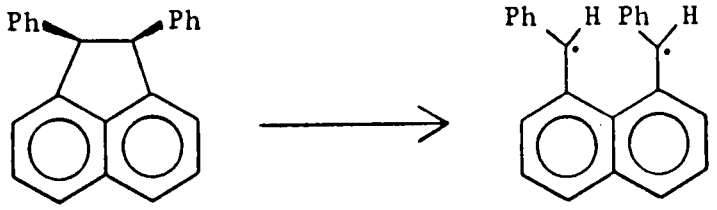
Another advantage in using the diphenyl analog is that the phenyl groups provide the necessary stereochemical markers for determining if reaction is taking place. Specifically, beginning with either the cis (135) or trans (136) compound, reaction is expected to cause at least partial formation of the other isomer as shown in Equation 37.



(37)

135 145 136

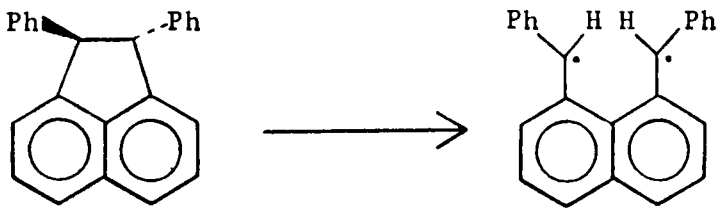
Prolonged photolysis of the cis compound in carbon tetrachloride or benzene failed to produce any of the trans isomer. Reaction of some type did occur in carbon tetrachloride as was noted by the disappearance of the benzyl proton signal in the nmr spectrum, but the product spectrum was not readily interpretable. The absence of cis-trans isomerization here may be indicating that the preferred direction of ring opening is the conrotatory mode. Such a process for the cis isomer would lead to the highly strained E,Z isomer (146) of the quinodimethane, which may make the reaction energetically forbidden.



(38)

135 146

If this hypothesis is correct, reaction might be expected to occur with the trans isomer whose conrotatory ring opening would lead to the more stable Z,Z isomer (145) of the quinodimethane. However, photolysis of 136 in benzene also failed to produce isomerization. It appears that the ring opening reaction requires more energy than is being provided by the photolysis light source.

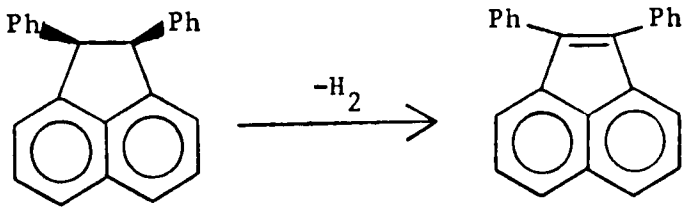


(39)

136 145

Bauld and Hudson[53] had previously attempted thermal isomerization of the cis compound. They found, though, that after heating it in diethyl phthalate at 275° C for ten hours, none of the trans isomer was present.

To determine if the reaction could be induced under more severe thermal conditions, a sample of the solid cis compound in an evacuated tube was heated in the flame of a Bunsen burner. (The temperature may be estimated at <820° C, the softening temperature of the glass tube.) The originally colorless material turned red during the heating. After cooling, an nmr spectrum of the tube contents indicated total conversion of the cis compound to the trans isomer. Also, by means of thin-layer chromatography, it was determined that the red color was due to the presence of 1,2-diphenylacenaphthylene (126), which would arise by hydrogen elimination from the starting material.

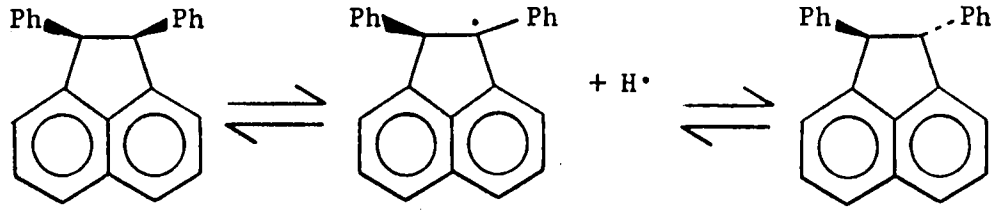


(40)

135 126

Similar heating of the trans compound produced a small amount of the cis isomer and again gave some diphenylacenaphthylene. A mass spectrum of the product mixture was obtained to determine if any dimeric products were being formed, but none was indicated.

It should be pointed out that although cis-trans isomerization is observed here, there is no evidence that the quinodimethane is the intermediate in the process. For example, one alternate mechanism that would give the same results as those observed involves hydrogen atom abstraction-recombination, as illustrated in Equation 41.

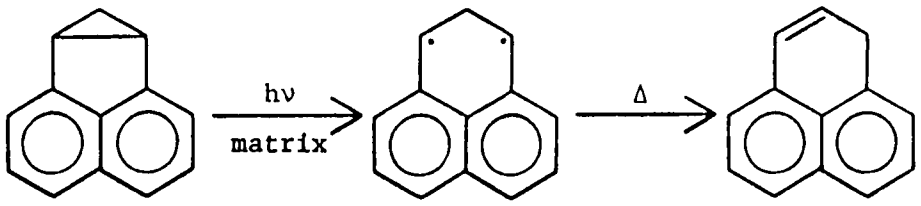


(41)

135 147 136

D. Thermal Generation of (1)1,8-NQM

Michl et al.[57] have demonstrated that photolysis of 6b,7a-dihydro-7H-cycloprop[a]acenaphthylene (124) in a rigid matrix at low temperature leads to the formation of (1)1,8-NQM (113), which thermally isomerizes quantitatively to 1H-phenalene (115).



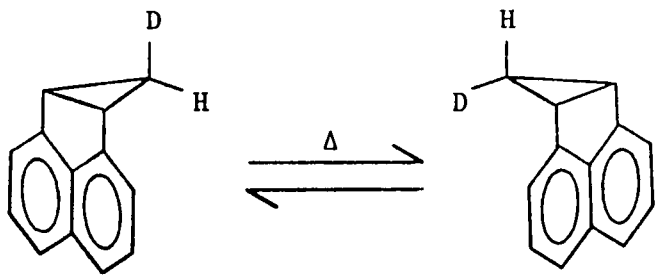
(42)

124 113 115

In this laboratory a solution of 124 in benzene-d_6 was photolyzed at room temperature; and although a reaction of the cyclopropane did occur, as monitored by nmr spectroscopy, no phenalene was produced. Subsequent flash photolysis of 124 by Wirz (private communication) indicates that the formation of the quinodimethane from the cyclopropane is a two-photon process. Thus, in solution at room temperature where the lifetimes of the intermediates are short, a two-photon process is highly unlikely.

In order to determine if the thermal rearrangement of the cyclopropane to phenalene also occurs via the NQM intermediate, it was proposed to prepare the exo-deuterio analog of the cyclopropane (91) and to note the position of the deuterium in the product after thermolysis. If the reaction were concerted, one would expect either D or H migration while a nonconcerted process would probably show some migration of each.

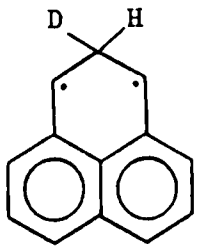
It was discovered that this experiment had already been performed by Roth and Enderer.[51] They found that heating 91 above ~130° C leads to rapid equilibration of the deuterium between the exo and endo positions of the cyclopropane, much faster than the formation of phenalene. This finding indicates that a biradical intermediate is



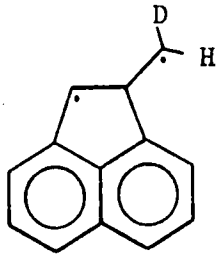
(43)

91 93

present during the reaction. Two may be proposed, arising either from cleavage of the internal cyclopropane bond to give the quinodimethane 92 or from cleavage of an external bond to give 148. Three arguments may be presented in support of the quinodimethane.



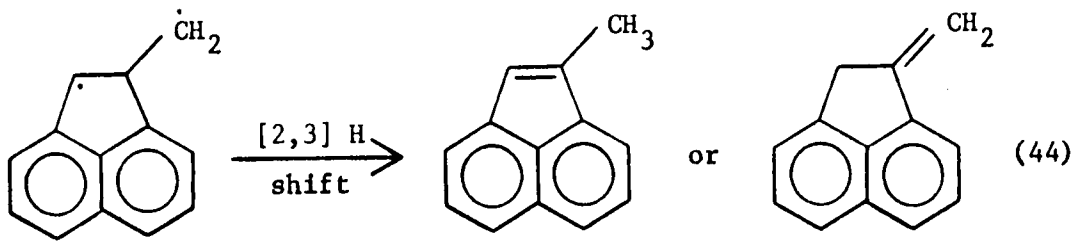
92



148

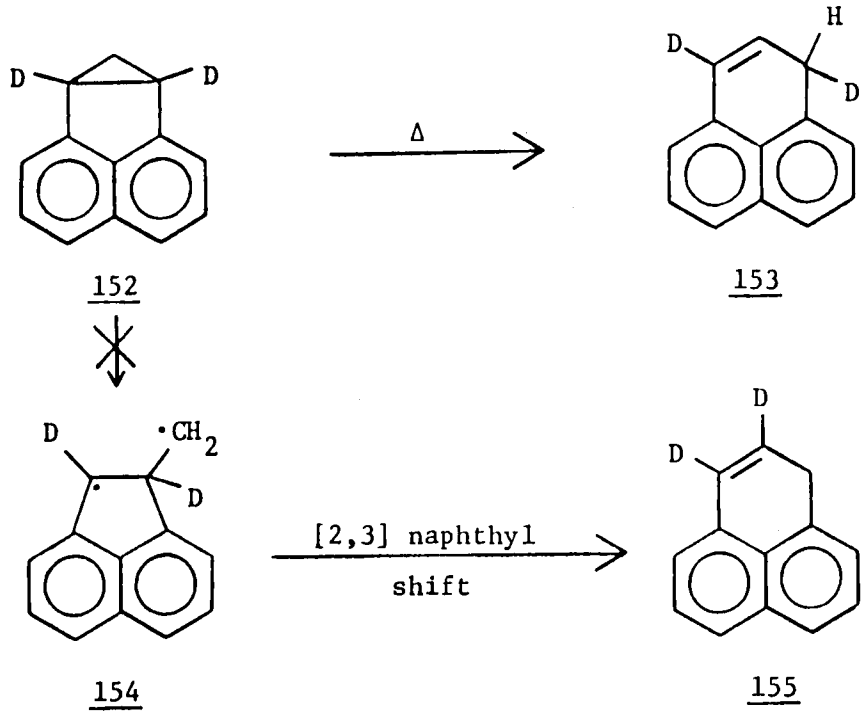
First, calculation of the enthalpies of reaction by the Benson method[64] indicates that the quinodimethane should be preferred. ΔH_r° for the formation of (1)1,8-NQM, with its two benzylic radical centers, from the cyclopropane is calculated at ∿19 kcal mol^{-1} while the value for the formation of 148, with one benzylic and one primary radical center, is ∿40 kcal mol^{-1}.

Secondly, if 149 (the nondeuteriated equivalent of 148) were being produced, one would expect the occasional formation of products such as 150 or 151, arising from a [2,3] hydrogen shift in the intermediate. At no time has either of these products been observed.



149 150 151 (44)

Lastly, if 149 were the species from which 1H-phenalene arises in the reaction, a [2,3] naphthyl shift in the intermediate could account for its formation. This mode of reaction can be ruled out, though, based on the finding that thermolysis of the dideuteriocyclopropane 152 yields phenalene with the deuterium atoms only in the 1 and 3 positions (153). A mechanism in which the equivalent of 149 were in fact the intermediate would result in the deuterium atoms occupying positions on carbons 2 and 3 (155).

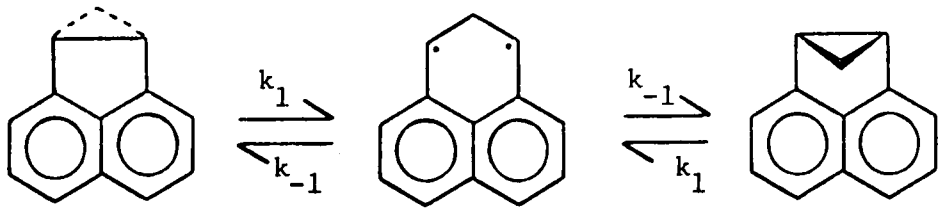


(45)

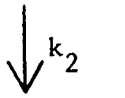
Thus it is apparent that (1)1,8-NQM is the actual intermediate in the cyclopropane thermolysis. The chemistry of this species produced thermally in solution, in which both ring closure and a [2,3] H shift may occur, is in marked contrast with the chemistry observed when it is produced photochemically in a matrix, in which only the hydrogen shift was found to occur.[57] A possible explanation for this

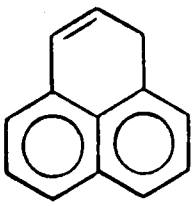
fact is that, depending on how it is generated, the quinodimethane is being produced in states with different multiplicities with each exhibiting its own particular chemistry. More detail on this idea will be presented later.

Having found that (1)1,8-NQM has two reaction pathways available to it in solution, it is desirable to determine and compare their relative rates, i.e., the ratio $k_{-1}:k_2$ as defined in Equation 46.



124 113 124





115

(46)

The first order reaction rates for the rearrangement of 124 to 115 were determined at three temperatures, and these are given in Table II. From these, the activation parameters for the process were calculated to be: $E_a = 34.7 \pm 2.1$ kcal mol^{-1}, log A = 13.2 ± 2.2, $\Delta H^{\neq} = 33.8 \pm 2.1$ kcal mol^{-1}, and $\Delta S^{\neq} = -0.7 \pm 5.0$ eu.

TABLE II

EXPERIMENTAL REACTION RATES FOR THE ISOMERIZATION OF 6b,7a-DIHYDRO-7H-CYCLOPROP[a]ACENAPHTHYLENE TO 1H-PHENALENE

Temperature (° C)	Rate (s^{-1})
140	9.68×10^{-6}
155	2.85×10^{-5}
170	1.66×10^{-4}

How are the observed reaction rates related to the rate constants defined in Equation 46? The disappearance of 124 with time is indicated in Equation 47. This equation can be made independent of

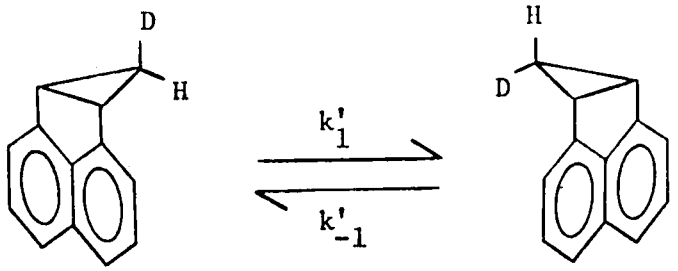
$$-\frac{d[124]}{dt} = 2k_1[124] - 2k_{-1}[113] \qquad (47)$$

the concentration of the intermediate 113 if the steady-state approximation is assumed. Thus, Equation 47 reduces to Equation 48 (see

$$-\frac{d[124]}{dt} = \frac{2k_1k_2}{2k_{-1} + k_2}[124] \qquad (48)$$

Appendix), from which the observed rates are seen to be proportional to $2k_1k_2(2k_{-1} + k_2)^{-1}$.

Roth and Enderer[51] investigated the kinetics of the thermal equilibration of compounds 91 and 93 and obtained the rate expression for the sum $k_1' + k_{-1}'$, defined in Equation 49. Assuming $k_1' \simeq k_{-1}'$, the



91 93 (49)

rate constant k_1' at a given temperature is given by Equation 50.

$$2k_1' = 8.4 \times 10^{14} \exp[-(35.0 \pm 0.5) \text{ kcal/RT}] \text{ s}^{-1} \quad (50)$$

In order to make use of the Roth-Enderer data a correlation must be established between the rate constants of Equations 46 and 49, which have been defined differently. It can be shown (Appendix) that $2k_1' = k_1$. With this relationship established, it is now possible to estimate the ratio $k_{-1}:k_2$ from Equation 46.

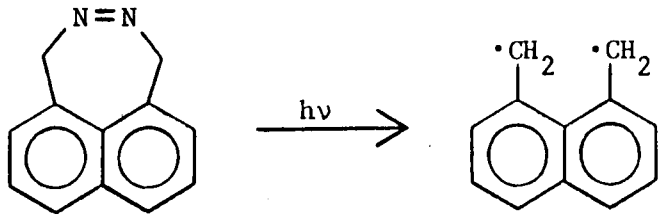
For 140° C, Equation 50 gives $2k_1' = k_1 = 2.52 \times 10^{-4}$ s^{-1}. Substitution of this value for k_1 into the rate expression for the cyclopropane isomerization at 140° C (Equation 51) gives a value for the ratio $k_{-1}:k_2$ of 25.5. Calculation of this ratio at the other temperatures studied with the inclusion of error limits gives an average value of 36 ± 19, indicating that ring closure occurs ∿36 times faster than the hydrogen shift.

$$\frac{2k_1k_2}{2k_{-1} + k_2} = 9.68 \times 10^{-6} \quad (51)$$

E. Spectroscopy of 1,8-NQM

1. Electron Spin Resonance Spectroscopy of (0)1,8-NQM

The electronic nature of (0)1,8-NQM, generated from the azo compound 89, was determined by electron spin resonance spectroscopy experiments performed by Dr. J. R. Dodd, then at Emory University.



(52)

89 83

Irradiation of a solution of 89 in hexafluorobenzene at 77 K with 300 nm light inside the probe of an esr spectrometer produced the spectrum shown in Figure 3. In addition to the strong radical resonance in the g = 2 region, resonance lines were observed at 3208.5, 3287.5, 3357.5, 3523.0, 3590.0, and 3675.5 G when the incident microwave frequency was 9.189 GHz. The six-line pattern is characteristic of a randomly oriented triplet species, lacking cylindrical symmetry and a cylindrical spin distribution. A weak resonance was also observed at 1703.4 G, which corresponds to the $\Delta m = 2$ transition of a triplet entity. The zero-field splitting parameters calculated from the observed spectrum are $D' = 0.0218\ cm^{-1}$ and $E' = 0.0021\ cm^{-1}$. These values correspond very closely to those obtained from the esr spectra of (1)1,8-NQM[57] and (2)1,8-NQM[54] (see Table III, p 59).

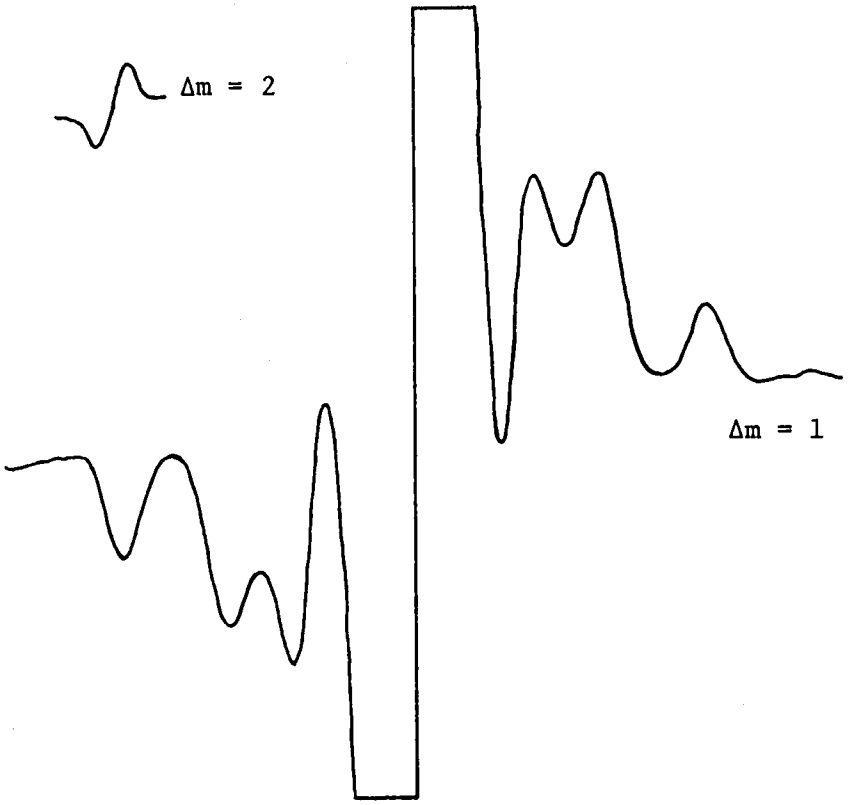


Figure 3. ESR spectrum of (0)1,8-NQM in hexafluorobenzene at 77 K.

To determine if the observed triplet was the ground state of (O)1,8-NQM or simply a low-lying excited state, a Curie law[65] study was proposed. In such a study, the intensity of the triplet esr signal is followed as a function of temperature. For a ground state triplet, the intensity (I) of the esr signal will vary inversely with the absolute temperature (T), giving a constant value to the product IT over the temperature range studied. On the other hand, if the observed triplet is an excited state lying at an energy (ΔE) above the ground state, then the intensity of the triplet signal will change as the populations of the ground and excited states vary over a range of temperatures. In this case the product IT is given by the expression in Equation 53.

$$IT = [\exp(-\Delta E/RT)][1 + 3\exp(-\Delta E/RT]^{-1} \qquad (53)$$

The Curie law study of (2)1,8-NQM had previously been conducted in the range 96-133 K.[54] In contrast to this species, the triplet esr signal of (O)1,8-NQM was found to decay rapidly upon raising the temperature as little as ten degrees above the 77 K where it was generated, precluding a Curie law study in this temperature range. Instead, using liquid helium as coolant, the esr signal intensities were studied as a function of temperature in the range 12.5-29.0 K. The experimental results were found to match those calculated for a system with a singlet ground state having a triplet excited state lying 45 ± 5 cal mol^{-1} above the ground state. This result along with those of (1)1,8-NQM[57] and (2)1,8-NQM[54] are presented in Table III.

TABLE III

ESR RESULTS FOR 1,8-NAPHTHOQUINODIMETHANES

System	D' (cm^{-1})	E' (cm^{-1})	$E_{T_1}-E_{S_0}$ (cal mol^{-1})
(0)1,8-NQM	0.0218	0.0021	45
(1)1,8-NQM	0.026	<0.002	640
(2)1,8-NQM	0.018	<0.003	200

2. Optical Spectroscopy of (2)1,8-NQM

Wirz et al.[66] have obtained the absorption and emission spectra of (2)1,8-NQM at 77 K, which are shown in Figure 4. The spectra are very similar to those previously published for (1)1,8-NQM[57] and show qualitative similarities to the as yet preliminary absorption spectrum of (0)1,8-NQM. Such similarities imply that the three species being observed have similar electronic properties, specifically the same electronic multiplicity. What is this multiplicity?

Table III shows that the energy gaps between the first excited triplet states and the singlet ground states of (0)1,8-NQM, (1)1,8-NQM, and (2)1,8-NQM are 45, 640, and 200 cal mol^{-1}, respectively. With such small energy gaps, except at very low temperatures the singlet and triplet states of the quinodimethanes should exist together in an equilibrium whose composition is determined by the temperature of the system. It is possible to calculate the relative amounts of the two states at a given temperature by using the Boltzman formula.

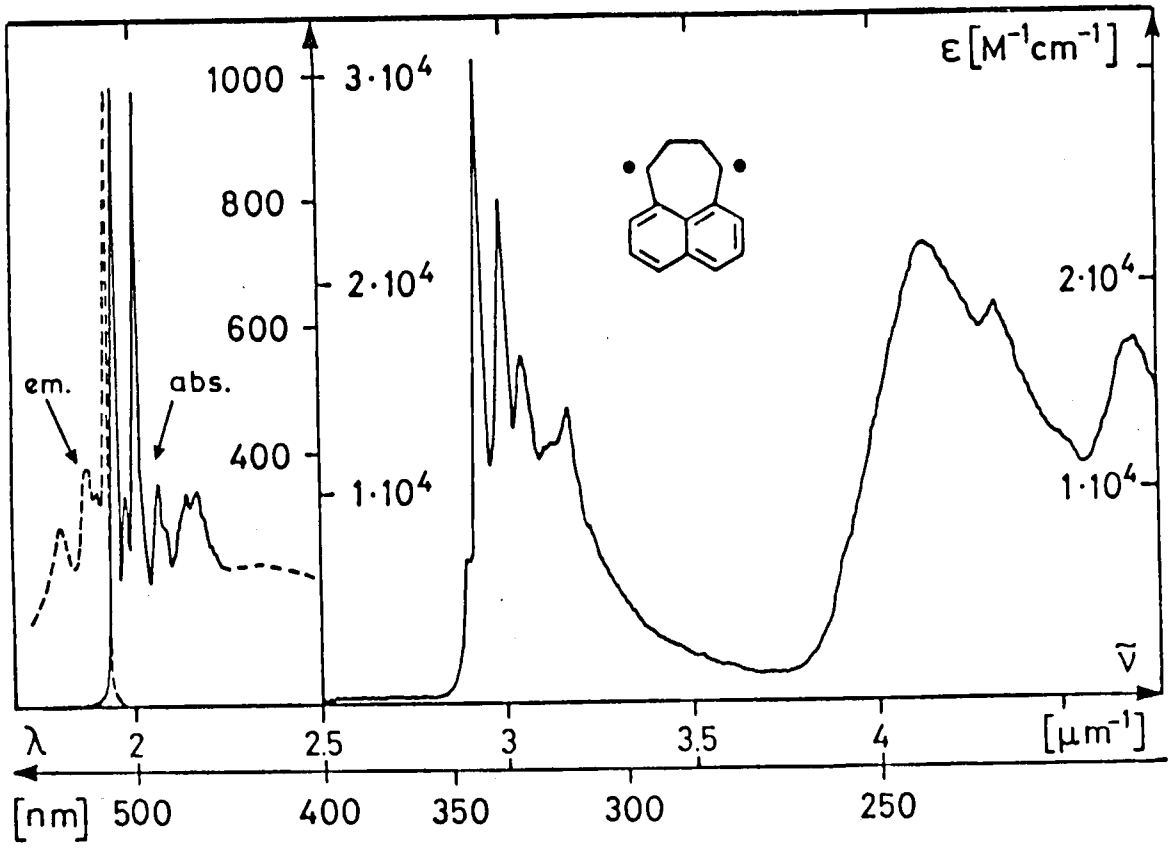


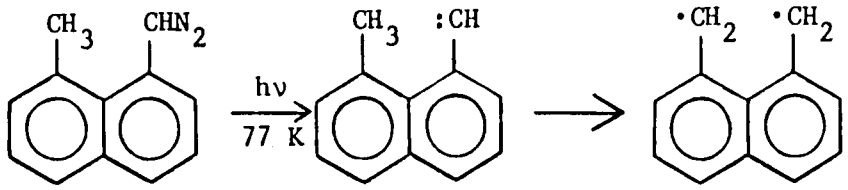
Figure 4. Absorption and emission spectra of (2)1,8-NQM in EPA at 77 K.

Thus, for the three systems just mentioned the singlet-triplet ratios at 77 K are calculated to be 0.5, 21, and 1.3, respectively. In other words, the singlet state of the quinodimethane is present in the equilibria to an extent of 33%, 95%, and 56%, respectively.

From these percentages, it is difficult to explain the similarity in the absorption spectra of (1)1,8-NQM and (2)1,8-NQM, when the former should be arising from essentially the lone singlet state species while in the latter case the spectrum arises from an almost equal mixture of the singlet and triplet states. Wirz et al.[66] investigated the absorption spectrum of (2)1,8-NQM over the temperature range 30-130 K to see what effect the variation in the singlet-triplet concentrations would have. Using the 200 cal mol^{-1} value for the S_0-T_1 energy gap, it may be calculated that the amount of singlet state present in the equilibrium would vary from 90% at 30 K to 42% at 130 K. Surprisingly, the shapes and intensities of the absorption bands did not vary over the temperature range studied. This finding is clearly inconsistent with a singlet-triplet mixture.

Suspecting that the earlier esr results may be incorrect, Wirz et al.[66] reinvestigated the temperature dependence of the esr spectra of (1)1,8-NQM and (2)1,8-NQM in the temperature range 4-77 K where the thermal population of an excited triplet state should become negligible. In both cases it was found that Curie's law was obeyed, indicating that the triplet states being observed were indeed the ground states. (A small deviation from Curie's law was noted for (2)1,8-NQM below 20 K.)

Platz[67] has recently generated (0)1,8-NQM by the process shown in Equation 54, which is apparently much more efficient in producing the quinodimethane than the azo decomposition described previously. For this case too, he found that the triplet was the ground state. Thus, in all three 1,8-NQM's the ground state is the triplet state, as was originally predicted by molecular orbital calculations.



(54)

156 157 83

Time-resolved esr spectroscopy experiments on the three 1,8-naphthoquinodimethanes are presently being conducted at Washington University under the direction of S. I. Weissman. Generating the biradicals within single crystals of their respective precursors, this technique can determine if they are initially produced in their triplet states and also from which triplet sublevel reaction occurs.

From the results presented thus far, it appears that the species responsible for the absorption spectrum of (2)1,8-NQM is the triplet ground state. One further piece of evidence that supports this conclusion is the fact that the observed spectrum is consistent only with that derived theoretically by open-shell PPP SCF CI calculations for triplet-triplet absorptions.[66]

Support for the validity of these calculations may be drawn from careful analysis of the optical spectra. Specifically, in spite of the near coincidence of the 0-0 absorption and emission bands at 512 nm, the two spectra lack mirror symmetry, which suggests that the absorption band consists of more than one electronic transition. The calculations in fact predict two transitions with opposite polarization in that region (509 and 486 nm).

Wirz et al.[66] successfully resolved the two component absorptions by the method of photoselection, described by Albrecht.[68] A sample of (2)1,8-NQM, randomly oriented in a poly(methyl methacrolate) matrix at 77 K, was photolyzed with linearly polarized light. This irradiation selectively destroyed those biradical molecules having the proper orientation relative to the incident radiation for light to be absorbed. The molecules remaining after the photolysis then possessed some degree of orientation within the matrix. The absorption spectrum was taken parallel and perpendicular to the direction of photolysis, giving two distinct spectra, which are shown in Figure 5. One of these spectra can be seen to be an approximate mirror image of the emission spectrum.

F. Interaction of Oxygen with 1,8-NQM

1. (2)1,8-NQM

Wirz et al.[66] have also successfully observed (2)1,8-NQM as a transient intermediate following the flash photolysis of its azo precursor 103 in solution at room temperature. The same species is observed following both unsensitized and benzophenone-sensitized

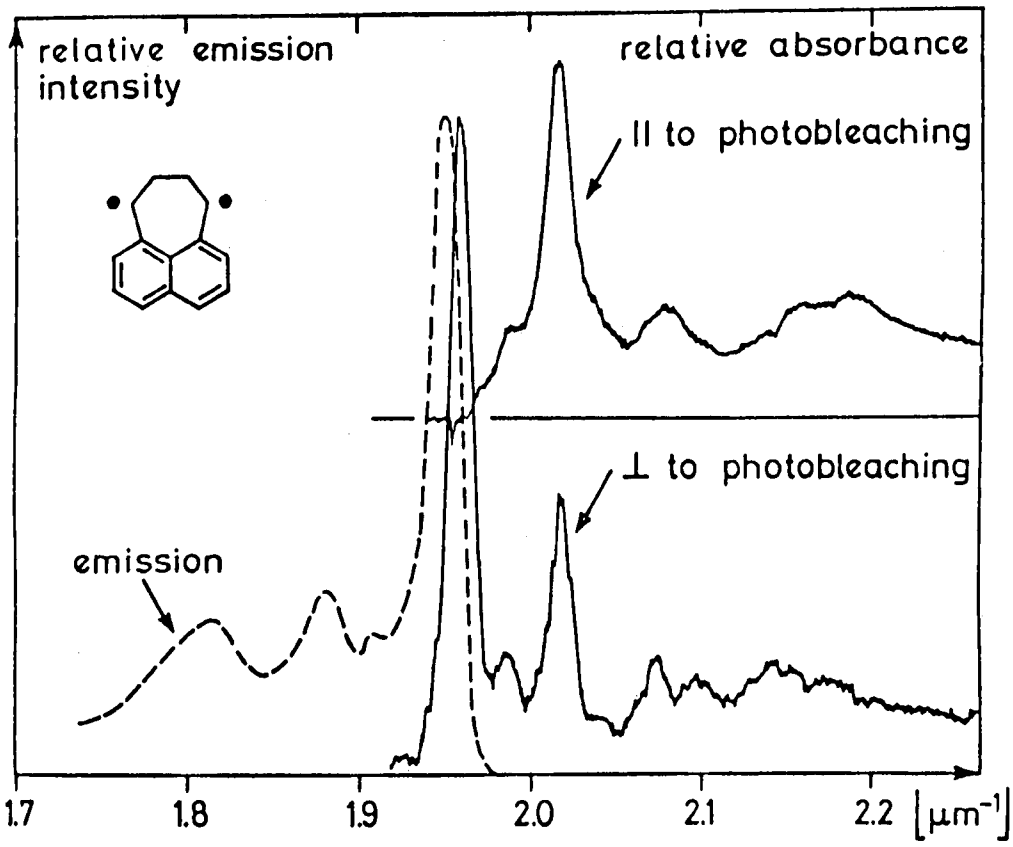
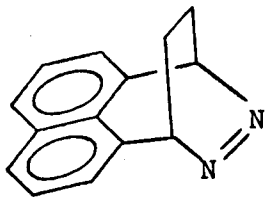


Figure 5. Resolved components of absorption spectrum of (2)1,8-NQM.

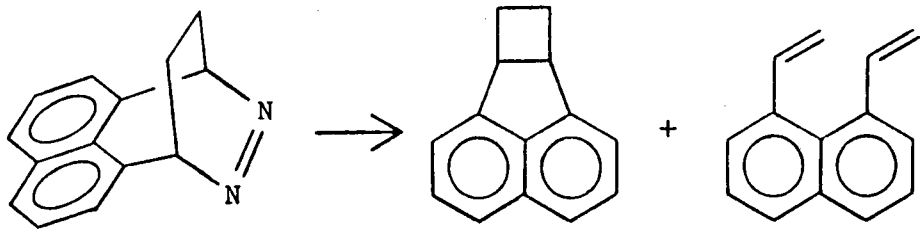
excitation of 103. The intermediate, which has a lifetime of 200 ± 20 μs in various solvents at 25° C, decays by a first order process which yields the Arrhenius parameters $A = 10^{6.9 \pm 0.3}\ s^{-1}$ and $E_a = 4.5 \pm 0.3$ kcal mol^{-1} (25-75° C in glycerol). Wirz ascribes the low value of the preexponential factor A (similarly, $A = 10^{4.5 \pm 1.0}\ s^{-1}$ for (1)1,8-NQM[57]) to a rate-determining step that involves a spin forbidden process, specifically intersystem crossing from the triplet ground state of the quinodimethane to its first excited singlet state from which the products arise.



103 → ^{3}(2)1,8-NQM → ^{1}(2)1,8-NQM* → products (55)

It was additionally noted that neither the yield nor the lifetime of the intermediate was affected significantly by the presence of dienophiles (trapping agents) or piperylene (triplet quencher). In contrast, the lifetime is dramatically reduced in the presence of oxygen or nitric oxide. In methanol, the bimolecular rate constants for quenching were found to be $(1.3 \pm 0.3) \times 10^{10}\ M^{-1}\ s^{-1}$ in the presence of oxygen and $(2.5 \pm 0.5) \times 10^{10}\ M^{-1}\ s^{-1}$ in the presence of nitric oxide, with both gases being partially consumed in the process. This last finding indicates that the gases are most likely trapping the intermediate to form some type of adduct.

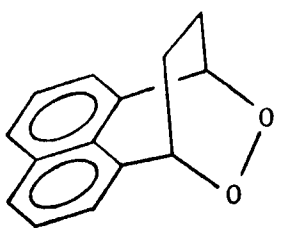
As described previously, both photolysis and thermolysis of the azo compound 103 in degassed solution leads to the formation of 104 and 105 in an approximate ratio of 7:1. In order to determine the effect of oxygen on this decomposition, a sample of the azo compound in benzene-d_6 was photolyzed while oxygen was bubbled through the solution. The nmr spectrum of the product mixture did not reveal the presence of any products other than the hydrocarbons. In order to determine the relative amounts of the two products, their nmr signals were integrated. Surprisingly, these results revealed a ratio of 104:105 of approximately 1:1. This ratio is far different from all results previously obtained in degassed solutions.



(56)

103 104 105

A mass spectrum of the product mixture showed a species with a mass corresponding to the peroxide 158, which is the possible structure for an adduct formed between oxygen and the intermediate quinodimethane. The amount of such an adduct could not be determined from



158

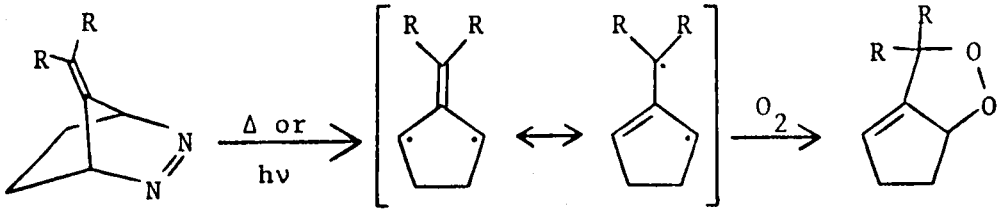
the mass spectrum; and because it was not apparently visible in the nmr spectrum, its yield was presumed to be low. By what mechanism is oxygen affecting this reaction?

One possible explanation is that oxygen traps the intermediate quinodimethane, and this adduct then decomposes under the reaction conditions to yield the same two hydrocarbons, but in a different ratio. Is such an idea, illustrated in Equation 57, plausible? In

$$\text{azo compound} \rightarrow (2)1,8\text{-NQM} \xrightarrow{O_2} \text{peroxide} \rightarrow \text{products} \qquad (57)$$

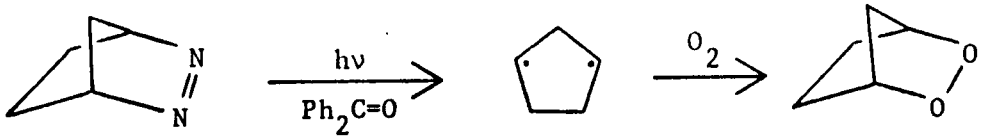
other words, should an oxygen adduct be produced during the azo decomposition; and once formed, would this adduct be expected to decompose to give the observed products?

Checking the literature, it was found that oxygen has recently been observed to trap the biradical intermediates of azo decompositions to produce peroxides. For example, Wilson and Geiser[69] successfully isolated compounds 162 (R = methyl, phenyl) and 165, which were produced as shown in Equations 58 and 59.



(58)

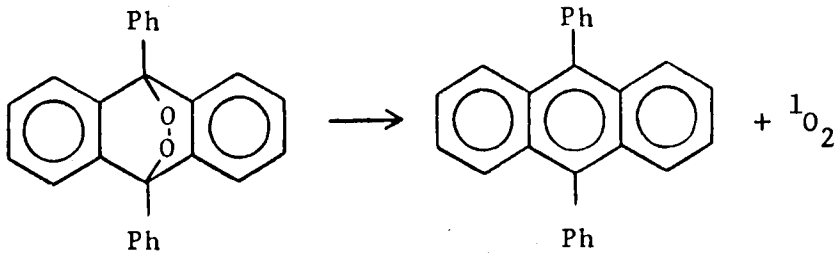
159 160 161 162



(59)

163 164 165

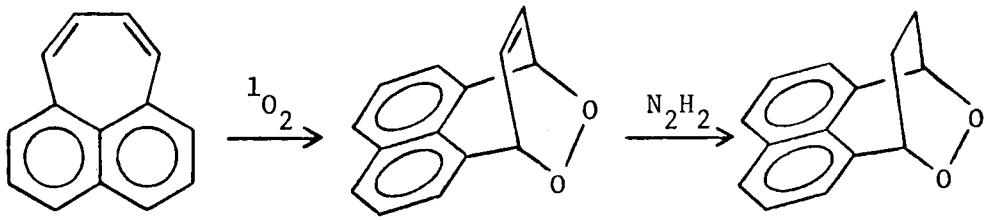
Oxygen elimination from a peroxide appears to be unlikely, however, since they normally decompose both photochemically and thermally by cleaving the O-O bond.[70] There are a few rare exceptions, though. Aromatic endoperoxides, such as the anthracene analog 166, do decompose thermally to produce the aromatic hydrocarbon and molecular oxygen in an excited singlet state.[71] Despite a qualitative similarity between 166 and the peroxide 158, the expected mode of decomposition of this peroxide is not at all apparent.



(60)

166 167

In order to go beyond speculation about how the peroxide 158 will decompose, it was proposed to prepare it and examine its photochemistry. The synthesis is shown in Equation 61.



(61)

117 168 158

The peroxidation step was accomplished by photolyzing a methylene chloride solution of cyclohepta[de]napthalene (117) containing a small amount of meso-tetraphenylporphine (sensitizer for

singlet oxygen) while oxygen was bubbled through. Initial attempts to run the reaction at room temperature resulted in the formation of polymeric material. This problem was overcome by cooling the reaction vessel in a dry ice-acetone bath during the photolysis.

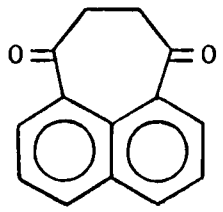
The reduction step was first attempted using direct catalytic hydrogenation which, not surprisingly, failed to give the desired product. Another failure occurred when the reducing agent diimide was generated in situ by the action of Cu^{2+} and hydrogen peroxide on hydrazine. Adam et al.[72] have successfully reduced a number of unsaturated peroxides with diimide produced by the reaction of acetic acid with excess dipotassium azodicarboxylate at low temperature. This method was found to work in the present case also, giving the crystalline peroxide.

An interesting discovery was made once an nmr spectrum of this peroxide was obtained--namely, that its nmr signals lay entirely under those of the hydrocarbons products of the azo decomposition. This could explain both the apparent absence of the oxygen adduct in the nmr spectrum following the oxygenated azo decomposition and the unusual ratio found for the two hydrocarbon products. Careful reexamination of that original nmr spectrum did reveal anomolous features which might be indicating that the peroxide was indeed present.

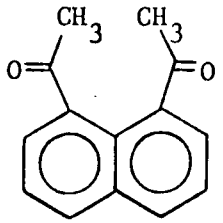
Having the peroxide in hand, it was photolyzed to determine if it would eliminate oxygen to give rise to the two products as the azo decomposition. It was first photolyzed under the same conditions as the azo compound ($\lambda \geq 380$ nm) and was found to be inert. Thus, if it

were being produced during the oxygenated azo decomposition, it would not undergo a secondary photolysis and disappear from the product mixture.

Next, the peroxide was photolyzed without light filtration. The material did disappear with time, as monitored by nmr spectroscopy, with the simultaneous appearance in the nmr spectrum of a singlet at δ 2.9 and a small multiplet at δ 8.5. No signals corresponding to the hydrocarbons 104 and 105 (p 66) were present. Infrared spectroscopy of the material revealed a band at ∿1690 cm^{-1}, indicative of an aromatic ketone, and the absence of a hydroxyl band. Possible structures for this product, arising from O-O bond breaking, are 169 and 170. No attempt was made to characterize this material further.



169



170

The goal of this work was to determine positively if oxygen does trap (2)1,8-NQM and, if so, to what extent. Since the 60 MHz nmr spectrometer was found to be inadequate for this task, the nmr spectrum of the products of the oxygenated azo decomposition was obtained on a 200 MHz spectrometer in operation at the University of South Carolina. (This work was sponsored by the National Science Foundation.) This spectrometer successfully resolved the product signals, and the peroxide 158 (p 68) was clearly present (Figure 6).

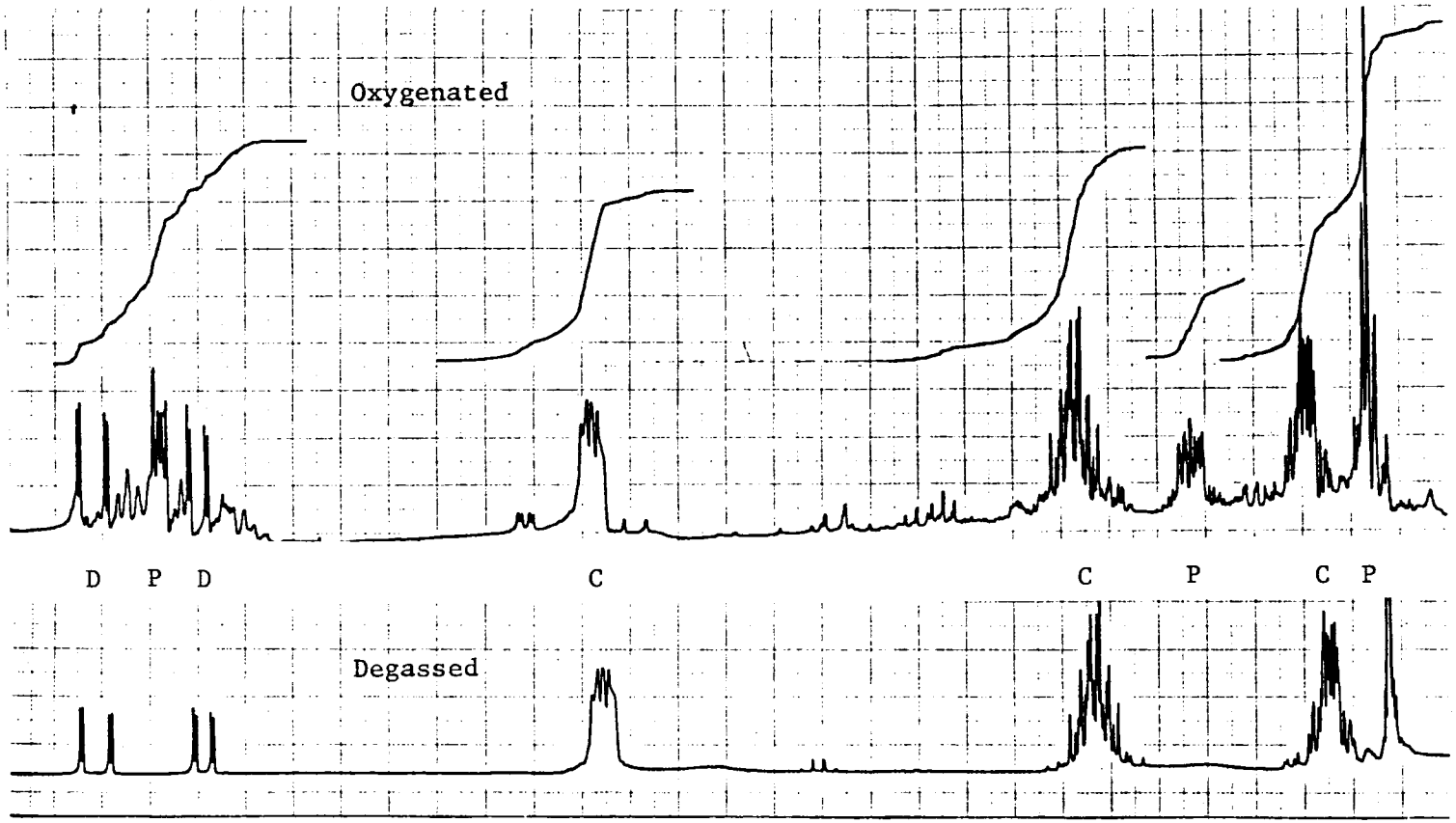


Figure 6. 200MHz nmr spectra of oxygenated and unoxygenated azo decompositions.

The aliphatic region of the spectra is shown. The high-field singlet is an impurity. The signals are labelled P for the peroxide, D for 1,8-diethenylnaphthalene, and C for 6b,7,8,8a-tetrahydrocyclobut[a]acenaphthylene.

Integration of the nmr signals revealed an approximate 27% yield of the peroxide 158 and a combined 73% yield of the two hydrocarbons 104 and 105 (p 66). (Extraneous signals in the nmr spectrum, possibly due to tube wobble from the tube being improperly sealed, prevented precise integration.) The relative yields of the two hydrocarbons were ∿78% 104 and ∿22% 105, roughly the same as found following degassed photolyses.

This ∿25% yield of peroxide was actually predicted prior to the experiment, based upon a theory known as spin statistics.[73] This theory was originally developed to explain the interaction of oxygen with excited aromatic triplet states. More recently it was invoked by Small and Scaiano[74] in their study of the interaction of oxygen with biradical intermediates generated in the Norrish II photofragmentation of phenyl alkyl ketones. For the four ketones studied, they had found that oxygen traps the intermediates ∿25% of the time. This theory will be described here as it would apply to the present chemistry.

The scheme to be presented rests on the assumption that quenching occurs via a collision complex of the biradical with molecular oxygen. For triplet NQM interacting with triplet oxygen, complexes can be formulated with quintet, triplet, and singlet multiplicities.

$$^3\text{NQM} + {}^3\text{O}_2 \longrightarrow \begin{cases} {}^5(\text{NQM}\cdots\text{O}_2) \\ {}^3(\text{NQM}\cdots\text{O}_2) \\ {}^1(\text{NQM}\cdots\text{O}_2) \end{cases} \qquad (62)$$

These multiplicities (S) are derived from the equation

$$S = 2S + 1, \tag{63}$$

in which S is given by

$$S = S_{NQM} + S_{O_2},\ S_{NQM} + S_{O_2} - 1,\ S_{NQM} - S_{O_2}, \tag{64}$$

where S_{NQM} and S_{O_2} are the sums of the electron spins of the quinodimethane (+1) and oxygen (+1), respectively. Assuming that spin-forbidden intersystem crossing between the three complexes is slow compared with any spin-allowed processes, each of the three complexes will exhibit its own chemistry. The chemistry will be of three types--dissociation back to initial reactants, dissociation to the NQM and oxygen in new spin states, or adduct formation.

In the case of the quintet complex, any chemistry other than reversion to the initial reactants would result in the formation of a species in a quintet state, i.e., ^5NQM, $^5O_2$, or ^5adduct. All of these spin-allowed products are of such high energies that their formation can be ignored. This leaves as the only reaction pathway available to the quintet complex the reversion to its components in their original spin states. Thus, this complex will not lead to any observable chemistry in the system although it will have an effect on the oxygen quenching rate, as will be described later.

$$^5(NQM\cdots O_2) \rightarrow \begin{cases} {}^5NQM + {}^1O_2 \\ {}^1NQM + {}^5O_2 \\ {}^5adduct \\ {}^3NQM + {}^3O_2 \end{cases} \tag{65}$$

In contrast, the triplet complex does appear to have an energy-allowed reaction pathway. The possible reaction paths are shown in Equation 66. The paths involving formation of $^1O_2$ and ^{3}adduct can be eliminated from consideration because too much energy would be required to produce these excited states. On the other hand, the formation of the excited singlet state of the quinodimethane is not expected to be as endothermic as the other two reactions, based on the belief that ^{3}NQM does indeed undergo intersystem crossing to ^{1}NQM from which the hydrocarbon products of the reaction arise (p 65). Oxygen could enhance this intersystem crossing by providing an allowed process in which electron spin is conserved. In this reaction, oxygen plays a purely catalytic role.

$$^3(\text{NQM}\cdots O_2) \begin{cases} \not\rightarrow\ ^3\text{NQM} + {}^1O_2 \\ \not\rightarrow\ ^3\text{adduct} \\ \rightarrow\ ^1\text{NQM} + {}^3O_2 \end{cases} \qquad (66)$$

Lastly, the singlet complex also has an energy-allowed reaction pathway other than reversion to starting materials. As before, the formation of singlet oxygen can be dropped from consideration, but the production of an NQM-oxygen adduct in a singlet ground state is very reasonable. This corresponds to the observed peroxide 158 (p 68).

$$^1(\text{NQM}\cdots O_2) \begin{cases} \not\rightarrow\ ^1\text{NQM} + {}^1O_2 \\ \rightarrow\ ^1\text{adduct} \end{cases} \qquad (67)$$

In summary, the interaction of ^{3}NQM with molecular oxygen is shown below. The probabilities of forming the three complexes are determined by the total number of each spin state produced. There will be five quintet states, three triplet states, and one singlet state. Thus, the probabilities of formation of the various complexes are 5/9 for the quintet, 3/9 for the triplet, and 1/9 for the singlet. Since the quintet state does not lead to any observable chemistry in the system, one would expect the hydrocarbon products and the adduct to be produced in a 3:1 ratio, and the quenching rate by oxygen should be approximately 4/9 of the diffusion-controlled rate.

$$^3\text{NQM} + {}^3\text{O}_2 \rightleftharpoons \begin{cases} {}^5(\text{NQM}\cdots\text{O}_2) \\ {}^3(\text{NQM}\cdots\text{O}_2) \rightarrow {}^1\text{NQM} \rightarrow \text{hydrocarbon products} \\ {}^1(\text{NQM}\cdots\text{O}_2) \rightarrow \text{peroxide} \end{cases} \quad (68)$$

The yield of peroxide was found to be ∿27%, well within the experimental error of the predicted 25%. Does the observed quenching rate then also support the theory? The exact rate of oxygen diffusion, on which to compare the observed quenching rate of 1.3×10^{10} M^{-1} s^{-1}, is unknown. However, it is at least 2.5×10^{10} M^{-1} s^{-1}, the value observed for nitric oxide quenching. The former value is approximately one-half of the latter. Is this result providing the answer to the question?

The ratio of the two hydrocarbon products of the azo decomposition is essentially unaffected by oxygen, indicating that their immediate precursor does not interact with oxygen in a significant

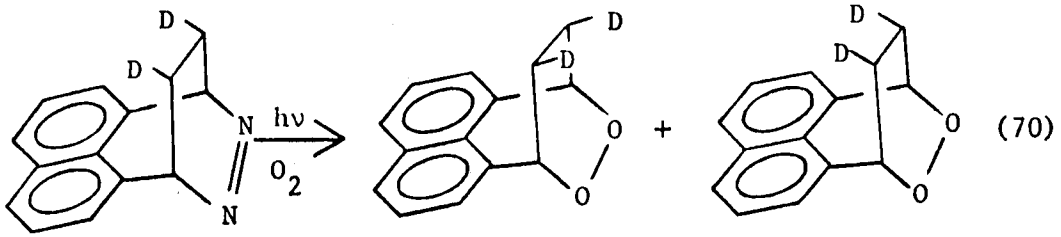
manner. It has been assumed that they arise from an excited singlet state of (2)1,8-NQM. Were this species to form a collision complex with oxygen in the manner described previously for the quinodimethane triplet state, the complex, a triplet species, is expected to be dissociative in nature. The formation of ^{3}NQM and $^3O_2$ is believed to be slow, as will be discussed, and any other chemistry would lead to products in excited states. Thus, this singlet precursor to the hydrocarbon products should not theoretically be affected by oxygen, as is observed. Alternatively, this singlet species may be too short-lived to be trapped by oxygen.

$$^1\text{NQM} + {}^3O_2 \rightleftharpoons {}^3(\text{NQM}\cdots O_2) \xrightarrow{\text{slow}} \begin{cases} {}^3\text{NQM} + {}^1O_2 \\ {}^3\text{NQM} + {}^3O_2 \\ {}^3\text{adduct} \end{cases} \qquad (69)$$

It should be noted, though, that the singlet species referred to above may not truly correspond to an energy minimum in the potential energy surface for the reaction and would not, by strict definition, be termed a reaction intermediate. At the same time, however, the descriptions presented which assume an excited singlet state of (2)1,8-NQM to be the reaction intermediate will not affect the logic of the arguments presented.

As discussed at the beginning of this chapter, when the azo compound stereospecifically labelled with deuterium atoms was decomposed, the labels were distributed in the hydrocarbon products in such a way

as to imply a planar or plane-averaged geometry for the reaction intermediate.[54] The reaction was repeated in the presence of oxygen to note its effects, if any. Decomposition of the azo compound 171, yielded the hydrocarbons with the same deuterium distribution as observed before (compounds 107-110, p 32). Due to the presence of deuterium atoms in these products, the nmr spectrum was less complex than in the nondeuteriated case, allowing the peroxide signals to be resolved. Analysis revealed that the deuterium atoms were distributed in the peroxide in equal amounts syn (172) and anti (173) to the oxygen atoms. This finding again indicates that the reaction intermediate has a planar geometry or conformations which average to a planar geometry more rapidly than oxygen can trap it.



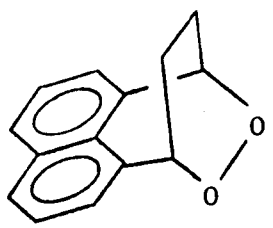
(70)

171 172 173

Less work was performed on the interaction of oxygen with (2)1,8-NQM generated thermally. The azo compound 103 (p 66) had previously been decomposed at 140° C in air,[54] and the reaction was repeated at 160° C with oxygen deliberately bubbled through the solution during the reaction. In neither case was anything unusual observed in the nmr spectrum.

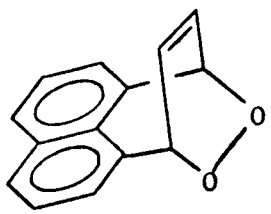
From labelling studies, it is known that (2)1,8-NQM is the reaction intermediate in the thermal azo decomposition.[54] Why then is it not trapped by oxygen? It may be that thermal nitrogen elimination from the azo compound 103 (p 66) leads directly to the intermediate in the singlet state from which the hydrocarbon products arise. As was just described, oxygen interaction with this singlet species should not give rise to an adduct unless the collision complex $^{3}(NQM\cdots O_2)$ produced from ^{1}NQM and oxygen dissociates to give ^{3}NQM (Equation 69, p 76). Since an oxygen adduct is not observed in this thermal reaction, the conclusion must be that the triplet state of the quinodimethane is not present during the reaction. One alternative explanation for the absence of an oxygen adduct is that the solubility of oxygen under the reaction conditions is too low for interaction to occur.

To see if oxygen elimination from the peroxide 158 would occur thermally, a sample of 158 in benzene-d_6 was heated at 150° C for 24 hr. Surprisingly, no reaction took place at this temperature, but reaction was observed at 180° C. Although the product nmr spectrum was different from the one taken after photochemical decomposition, neither of the hydrocarbons 104 or 105 (p 66) was apparent in the spectrum. Thin-layer chromatography confirmed their absence.



158

Before closing this section, two further experiments will be described. The unsaturated peroxide 168 was decomposed both photochemically and thermally to see if it would eliminate oxygen, giving cyclohepta[de]naphthalene (117). The nmr spectra from the two reac-



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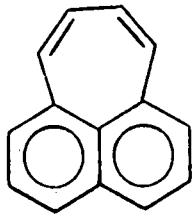
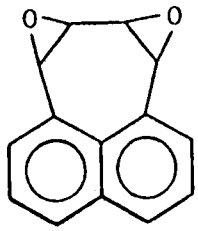


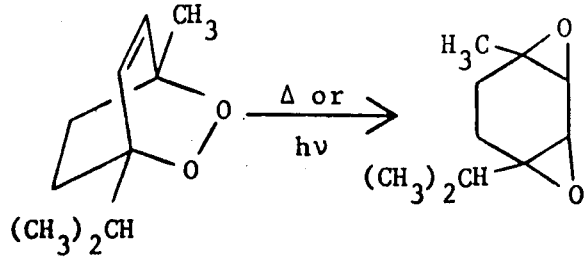
117

tions were identical and did not reveal any 117. Its absence was confirmed by thin-layer chromatography. The spectra were not readily interpretable, but O-O bond scission might lead to the diepoxide 174.



174

A similar reaction has been observed for the peroxide 175, for example.[75]

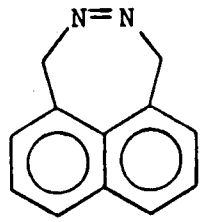


(71)

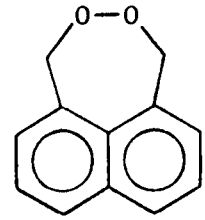
175 176

2. (0)1,8-NQM

A sample of 89 was photolyzed in benzene-d_6 while oxygen was bubbled through the solution. Nothing other than acenaphthene was present in the nmr spectrum of the product. Since reaction of oxygen with the triplet state of (0)1,8-NQM would be expected if the species is not too short-lived, the absence of an oxygen adduct lends support to the belief that the quinodimethane, at least its triplet state, is not an intermediate in this reaction. Were an adduct to form, a possible structure for it would be 177.

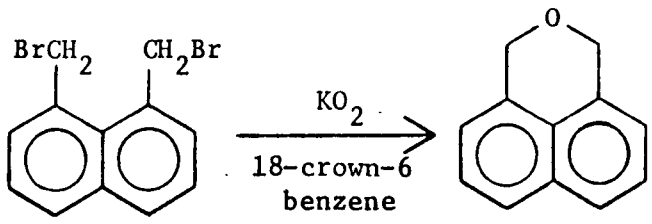


89



177

Prior to the synthesis of the bridged peroxide described in the previous section, it was proposed to prepare 177 to use as a model compound. The method employed was that of Johnson and Nidy,[76] who had found that superoxide reacts with alkyl halides to give peroxides. Thus, 1,8-bis(bromomethyl)naphthalene (130) was treated in benzene with potassium superoxide, using a crown ether to solubilize the ionic compound. Analysis of the product revealed the pyran 178 to be the



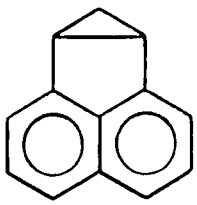
(72)

130 178

major product, with the peroxide present in a very minor amount, as indicated by the mass spectrum. How the pyran is produced in this reaction is not clear; but since it was not the desired product, the reaction was not further investigated. It is mentioned here only because of the current interest in superoxide and singlet oxygen chemistry, and this may represent a new reaction of superoxide.

3. (1)1,8-NQM

A sample of 124 in bromobenzene was heated at 140-150° C while oxygen was bubbled through the solution. The nmr spectrum of the product revealed no unusual signals, and a mass spectrum showed no products with masses corresponding to that of an oxygen adduct. The explanation for this result may well be the same as that described for (2)1,8-NQM generated thermally--the intermediate is most likely being produced directly in its singlet state which does not form an adduct with oxygen.



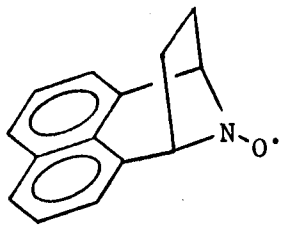
124

As was mentioned previously, Wirz has found that photochemical generation of (1)1,8-NQM from 124 is a two-photon process, precluding the reaction being conducted in solution at ambient temperatures. Thus, an experiment to react oxygen directly with the triplet state of the quinodimethane could not be performed.

G. Interaction of Nitric Oxide with 1,8-NQM

1. (2)1,8-NQM

During flash photolysis experiments, Wirz et al.[66] found that nitric oxide quenches the triplet state of (2)1,8-NQM at or close to the diffusion-controlled rate and appears to trap the intermediate to some extent. Maruthamuthu and Scaiano[77] have recently observed nitric oxide trapping of the triplet biradicals produced in the Norrish I photocleavage of cycloalkanones to give nitroxide radicals. Similar trapping in the present case would lead to an adduct with the structure of compound 179. Since nitric oxide has an odd number of electrons, the nitroxide 179 would also possess an odd electron. This feature should make the species amenable to detection via its esr spectrum.



179

The simplest esr spectrum of 179 would consist of a 1:1:1 triplet, resulting from the interaction of the nuclear spin of nitrogen with the spin of the odd electron. If there is additional splitting of the signals due to interaction of the electron spin with the proton nuclear spins, the spectrum will be more complex but should retain the basic triplet pattern.

A sample of the azo precursor to (2)1,8-NQM (103, p 66) in benzene-d_6 was photolyzed while nitric oxide was bubbled through the solution. The nmr spectrum of the product revealed the formation of the normal hydrocarbon products (104 and 105, p 66) in what appeared to be their typical ratio. (Their total yield was very low, and integration of the nmr signals was not possible.) No definite signals belonging to a nitric oxide adduct could be discerned. This, however, would be expected since the interaction of an odd electron spin with proton nuclear spins often causes line broadening in the nmr spectrum.

An esr spectrum of the product is shown in Figure 7. This totally unexpected five-line spectrum with its intensity pattern of 1:2:3:2:1 is indicative of the interaction of a free electron with two magnetically equivalent nitrogen atoms. A mass spectrum of the product revealed a species with a molecular weight corresponding to an adduct formed between the quinodimethane and two molecules of nitric oxide.

Such an adduct would have an even number of electrons and thus not give an esr spectrum. The observed spectrum must then be arising from a radical cation or radical anion of the adduct. This is not unreasonable since nitric oxide has a relatively low ionization potential,[78] and electron transfer between the adduct and nitric oxide might occur, giving the radical anion of the adduct. The species responsible for the esr spectrum probably has the structure 180.

In a control experiment, nitric oxide was bubbled through a solution of 103 at room temperature without photolysis. The solution became dark brown, and its esr spectrum was taken (Figure 7). A five

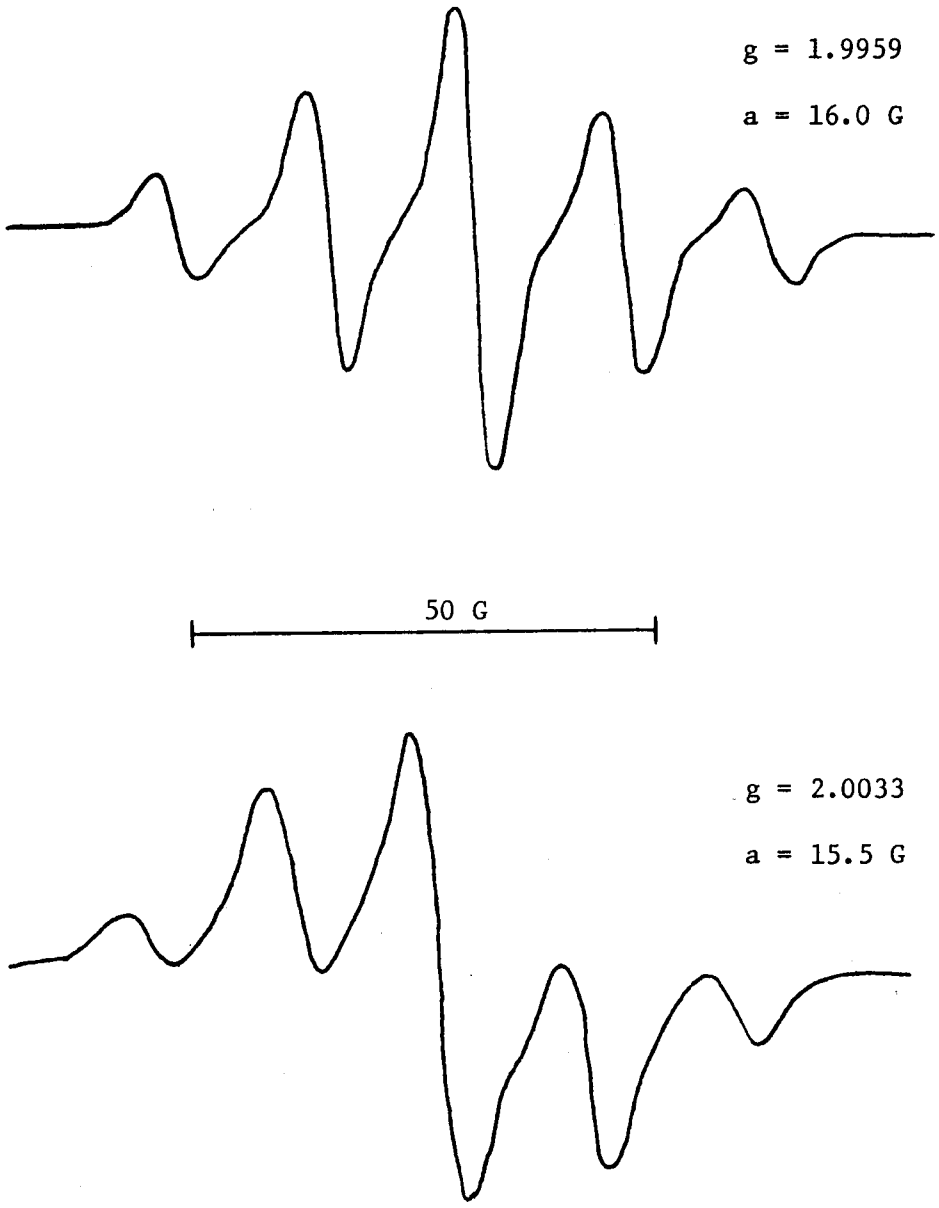
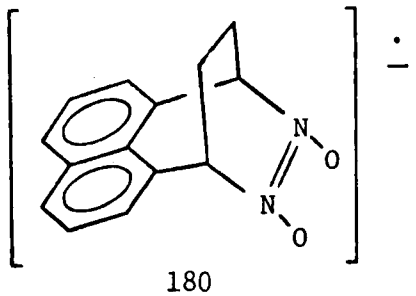


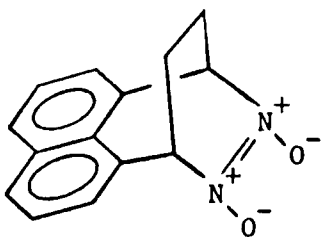
Figure 7. ESR spectra of photolyzed (top) and unphotolyzed (bottom) solutions of azo compound 103 through which nitric oxide was bubbled.



180

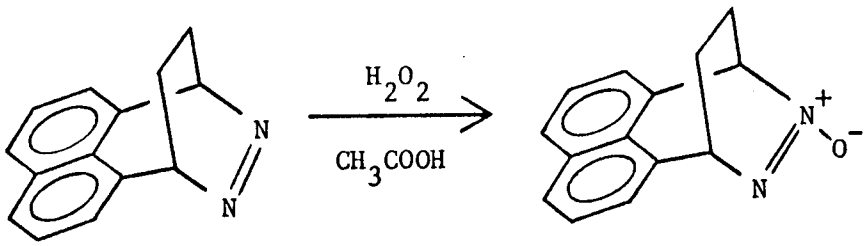
line spectrum very similar to the one obtained previously was observed. This finding indicates that electron transfer occurs between nitric oxide and the azo compound. Although the positions and coupling constants of the two spectra are almost identical, the intensity patterns are not quite the same. The two are most likely arising from two different species, but this cannot be said with absolute certainty. Despite this, the existence of the nitric oxide adduct is confirmed by the mass spectrum.

To confirm the structure of this adduct, it was proposed to synthesize the azo dioxide 181, bubble nitric oxide through a solution of the compound, and see if the same esr spectrum is obtained from this solution as from the photolysis. Azo dioxides can be prepared in some cases by oxidation of the appropriate azo compound. Snyder, Heyman, and Suciu[79] have successfully used peracetic acid as the oxidizing agent.



181

In a first attempt, a sample of 103 was refluxed in a solution consisting of equal volumes of acetic acid and 30% hydrogen peroxide. Workup unfortunately revealed that under these somewhat vigorous reaction conditions, the organic species was totally destroyed. The reaction was then repeated except the reagents were simply stirred overnight at room temperature. An nmr spectrum and mass spectrum of the product obtained revealed it to be the azoxy compound 182.



(73)

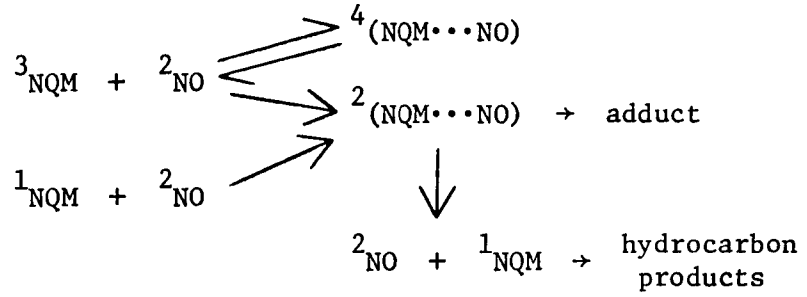
103 182

In one final attempt, the azoxy compound 182 was heated at 60° C in the acetic acid-hydrogen peroxide mixture. A mass spectrum showed that the oxidizing agent worked slowly on the starting material at this temperature, but numerous oxidation products were afforded. The synthesis was abandoned because it appeared that the reaction conditions required to place the second oxygen atom on the azo compound would also oxidize the aromatic nucleus. In none of the azo dioxides prepared by Snyder, Heyman, and Suciu[79] were any aromatic rings present.

The azo compound 103 in bromobenzene was heated at 140-150° C while nitric oxide was bubbled through the solution. An esr spectrum of the product was identical to the one obtained from the photochemical reaction. Based on the arguments presented in the previous

section, this indicates that nitric oxide interacts in an identical manner with the triplet state of (2)1,8-NQM, produced in the photochemical reaction, and with the quinodimethane singlet state, produced in the thermal reaction. Is this reasonable?

If the assumption that nitric oxide interacts with (2)1,8-NQM via a collision complex is correct, spin statistics can provide the answer. For triplet NQM interacting with doublet nitric oxide, two complexes can be formulated with quartet and doublet multiplicities. Since any products derived from the quartet complex would be formed in high energy excited states, the only energy-allowed reaction pathway for it would be reversion to the quinodimethane and nitric oxide in their original spin states. This leaves the doublet complex as the precursor to both the hydrocarbon products of the reaction, via the spin-allowed formation of ^{1}NQM, and the adduct.

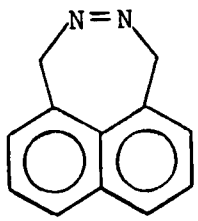


(74)

For singlet NQM interacting with doublet nitric oxide, only one collision complex can be formulated; and it will have doublet multiplicity, the same complex as is produced from ^{3}NQM. Thus, identical results should be observed from the interaction of nitric oxide with both the singlet and triplet states of (2)1,8-NQM.

2. (0) 1,8-NQM

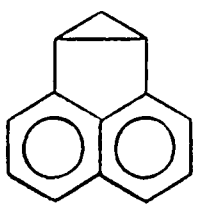
A sample of 89 in benzene-d_6 was photolyzed while nitric oxide was bubbled through the solution. An esr spectrum of the product is shown in Figure 8, along with the spectrum of a control in which the gas was bubbled through a solution of the azo compound at room temperature without photolysis. In this case, it is quite clear that the spectra are due to two different species. The many-lined spectrum is not readily interpretable, but it does indicate that nitric oxide has trapped some species during the course of the photolysis.



89

3. (1) 1,8-NQM

A sample of 124 in bromobenzene was heated at 140-150° C while nitric oxide was bubbled through the solution. No esr spectrum was obtained from the product, indicating that either no adduct was produced or that it was diamagnetic. This latter case would be



124

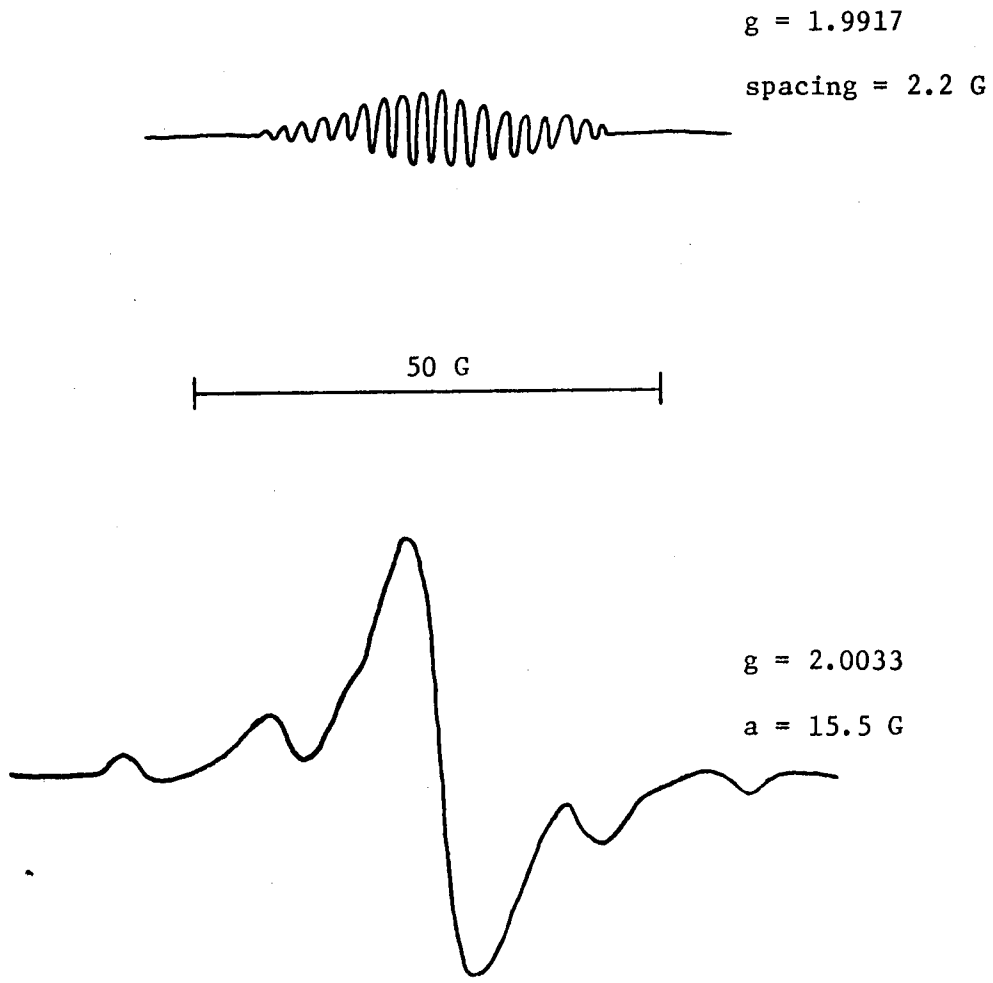
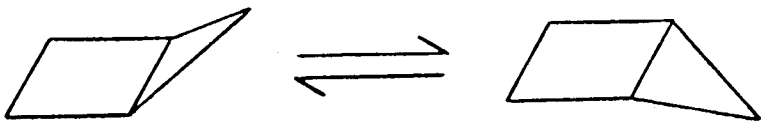


Figure 8. ESR spectra of photolyzed (top) and unphotolyzed (bottom) solutions of azo compound 89 through which nitric oxide was bubbled.

unusual based on the results of the other nitric oxide adducts. It is reasonable to expect the singlet state of (1)1,8-NQM to from an adduct in a similar manner as the singlet state of (2)1,8-NQM was found to do. The failure to observe an adduct may be indicating a fact, not previously considered, that there is in fact no true intermediate in the thermal reactions of the cyclopropane 124.

Despite all the arguments presented in support of the intermediacy of the quinodimethane, the results from all the experiments described can also be rationalized by concerted processes, without invoking a reaction intermediate. Even the epimerization of the deuterium-labelled cyclopropane does not necessarily indicate the presence of an intermediate. For example, Buchwalter and Closs[80] believe that there is no reaction intermediate in the isomerization of bicyclopentane 183, shown in Equation 75. More work will be necessary to confirm such a hypothesis in the present case.



183 183 (75)

H. Summary and Conclusions

1. (0)1,8-NQM

Of the three quinodimethanes investigated, the least is known about (0)1,8-NQM. It was found that photolysis (π,π^*) of 1,4-dihydronaphtho[1,8-de]diazepine (89, p 42) causes nitrogen elimination,

producing acenaphthene. The triplet state of the quinodimethane can be observed via its esr spectrum when the reaction is run in a matrix at low temperature. It is not clear to what extent, if any, (0)1,8-NQM plays a role in the room temperature reaction. Stereochemical studies which might give insight into this question were not performed. Oxygen failed to have an effect on the reaction, contrary to what spin statistics would predict if a reasonably long-lived triplet intermediate were present. Nitric oxide appears to have formed an adduct with an intermediate of this reaction, but its identity cannot be given with certainty. Lastly, isomerization of cis- and trans-1,2-diphenyl-1,2-dihydroacenaphthylene (135 and 136, p 46) at high temperature indicates a reaction intermediate, although again its exact nature is unknown.

2. (1)1,8-NQM

Photolysis of 6b,7a-dihydro-7H-cycloprop[a]acenaphthylene (124, p 49) in a matrix at low temperature gives rise to the triplet state of (1)1,8-NQM by a two-photon process. This species has been observed by both its esr and absorption spectra. Once formed, this quinodimethane undergoes a thermal [2,3] hydrogen shift to yield 1H-phenalene. The cyclopropane also yields phenalene upon thermolysis. Deuterium-labelling studies indicate that the cyclopropane undergoes epimerization faster than phenalene formation. Kinetics measurements, which assume (1)1,8-NQM to be an intermediate in the thermal reaction, reveal that ring closure occurs ∿36 times faster than the [2,3] hydrogen shift, forming phenalene. Failure of this intermediate to be trapped

by either oxygen or nitric oxide may indicate that it does not in fact exist, i.e., that both thermal processes are concerted.

3. (2)1,8-NQM

Both photolysis and thermolysis of 1,4-dihydro-1,4-ethanonaphtho[1,8-de]diazepine (103, p 31) lead to two products--6b,7,8,8a-tetrahydrocyclobut[a]acenaphthylene (104, p 31), the major product, and 1,8-diethenylnaphthalene (105, p 31), the minor. Deuterium-labelling studies indicate that (2)1,8-NQM is the intermediate in both of these processes and that the quinodimethane has a planar geometry or conformations that average to a planar geometry more rapidly than reaction occurs. The triplet ground state of the species has been observed via its esr and absorption spectra. The formation of an adduct between oxygen and the intermediate of the photochemical reaction in an ∿25% yield is interpreted by spin statistics as indicating that the reaction procedes via the triplet state of the intermediate. The fact that oxygen does not affect the ratio of the hydrocarbon products of the reaction indicates that they arise from the singlet state of the quinodimethane, which does not interact significantly with oxygen. This is confirmed by noting the absence of adduct formation in the thermal reaction, in which the intermediate is believed to be produced directly in the singlet state. Nitric oxide traps the intermediates of the photochemical and thermal reactions in an identical manner. Spin statistics again predict this result. From these results, which appear to fit the theory so nicely, it appears that the use of oxygen and nitric oxide as probes of biradical reaction intermediates holds great potential for further studies in the future.

CHAPTER III

EXPERIMENTAL SECTION

A. Analytical Techniques

Nuclear magnetic resonance (nmr) spectra were recorded on Varian T-60A and Nicolet TT14 spectrometers. Samples were run in carbon tetrachloride, chloroform-d, or benzene-d_6, using tetramethylsilane (TMS) as internal standard. Chemical shifts are reported as parts per million downfield from TMS in δ units. Nmr spectra are reported in the order: chemical shift (splitting, number of protons, coupling constants, assignment).

Electronic (uv) spectra were recorded on a Cary 17 spectrophotometer. Samples were run in 95% ethanol. Only the longest wavelength absorptions are reported.

Infrared (ir) spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer. Samples were run in benzene-d_6.

Electron spin resonance (esr) spectra were recorded on a Varian E-109 spectrometer. Samples were run in benzene-d_6 and bromobenzene.

Mass spectra were recorded on a Hewlett-Packard 5980A gas chromatograph-mass spectrometer. Samples were run as solids.

Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected.

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

B. Preparations of Compounds

1. 1*H*-Phenalen-1-one (114)

This material was prepared by a modification of the procedure of Watson et al.[54]

To 3 L of anhydrous ether were added 100 g (2.1 mol) of a sodium hydride oil dispersion (50% by weight hydride), 3 mL of ethanol, 170 g (1 mol) of technical grade acetonaphthone, and 148 g (2 mol) of practical grade ethyl formate. With vigorous stirring, the mixture was brought to reflux. After about 1 hr, the reflux rate increased sharply and heating was discontinued. A whitish solid precipitated in the flask as most of the ether boiled out. Following 30 min of additional stirring, 1.5 L of water was added to the flask to dissolve the solid. The aqueous solution was washed with three 500-mL portions of ether and then acidified with 200 mL of concentrated hydrochloric acid, causing precipitation of a white solid. The solid was extracted into 1 L of ether, which was dried with anhydrous magnesium sulfate and the solvent removed to give a red oily residue. This residue was diluted to 1 L with carbon tetrachloride and added dropwise to 1 L of a vigorously stirred 80% sulfuric acid solution, cooled in an ice-water bath.

Following the addition, 400-mL portions of the solution were each treated as follows. The aliquot was added to 1.5 L of water and 500 mL of carbon tetrachloride. The organic phase was collected, and the aqueous phase was twice more extracted with 500 mL portions of carbon tetrachloride. The organic extractions were combined, dried

with anhydrous magnesium sulfate, and the solvent removed, giving a rust-colored solid, which was air dried. The solid was chromatographed on alumina, eluting with ether. This afforded 141 g (78%; 97% based on an assumed 80% amount of 1-acetonaphthone in the technical grade starting material) of yellow 1H-phenalen-1-one. This material was used without further purification.

2. 1*H*-Phenalene (115)

This material was prepared by the procedure of Boudjouk and Johnson.[81]

Diisobutylaluminum hydride (32 mL of a 20% solution in hexane) was added dropwise over 30 min to a stirred solution of 4.0 g (22 mmol) of 1H-phenalen-1-one in 100 mL of benzene. The resultant solution was refluxed overnight. After cooling, the excess hydride was destroyed by the dropwise addition of saturated aqueous ammonium chloride until no further precipitation could be observed. Ligroin was added to the mixture, and the solid was removed by filtration. The solution was then washed with water and dried with anhydrous magnesium sulfate. Removal of the solvent gave a solid residue which was chromatographed on deactivated alumina, eluting with ligroin. The yield of slightly yellowish 1H-phenalene was 2.6 g (70%).

3. Cyclohepta[*de*]naphthalene (117)

This material was prepared by the procedure of Watson et al.[54]

To a solution of 3.40 g (20.5 mmol) of 1H-phenalene in 2.5 L of anhydrous ether, stirred under a nitrogen atmosphere at room temperature, was added 40 mL of 1.6 M n-butyllithium. After stirring 2 hr,

the solution was cooled to -78° C and 5.0 mL (77.5 mmol) of methylene chloride were added dropwise over 20 min, followed by 25 mL of 1.6 M n-butyllithium added dropwise over 30 min. The solution was returned slowly to room temperature and left to stir overnight. Distilled water (200 mL) was then added to destroy any remaining n-butyllithium. The ether solution was extracted with water and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporator; and the residue was chromatographed on alumina, eluting with ligroin. The material obtained was shown by nmr spectroscopy to be a mixture of 2,3-dihydro-1,2,3-metheno-1H-phenalene (116, p 35) and cyclohepta[de]-naphthalene in an approximate ratio of 5:1. In order to convert all of this material to the desired product, it was dissolved in 400 mL of ligroin saturated with iodine and left to stand at room temperature overnight. Chromatography on alumina, eluting with ligroin, afforded 1.43 g (39%) of cyclohepta[de]naphthalene.

4. 1,4-Dihydro-1,4-ethanonaphtho[1,8-*de*][1,2]diazepine (103)

This material was prepared by the procedure of Watson et al.[54] in a three-step synthesis, starting with cyclohepta[de]naphthalene.

a. Diethyl-1,4-ethenonaphtho[1,8-*de*][1,2]diazepine-2,3(1*H*,4*H*)-dicarboxylate (118). A solution of 3.34 g (19 mmol) of cyclohepta-[de]naphthalene and 3.70 g (20 mmol) of diethylazodicarboxylate in 80 mL of benzene was refluxed 24 hr. The solvent was removed by rotary evaporator, and the residue was chromatographed on deactivated alumina. Elution with 4% ether-96% ligroin removed unreacted cyclohepta[de]naphthalene, 20% ether-80% ligroin removed unreacted di-ethylazodicarboxylate, and 100% ether removed the desired adduct.

b. Diethyl-1,4-ethanonaphtho[1,8-*de*][1,2]diazepine-2,3(1*H*,4*H*)-dicarboxylate (119). The residue from part a was dissolved in 50 mL of 95% ethanol and placed in a Parr bottle with 80 mg of 5% palladium on powdered charcoal. After shaking 48 hr under a hydrogen atmosphere on a Parr hydrogenation apparatus, the solvent was removed after filtration through Celite.

c. 1,4-Dihydro-1,4-ethanonaphtho[1,8-*de*][1,2]diazepine (103). To the residue from part b dissolved in 35 mL of methanol was added 5 g of potassium hydroxide dissolved in 5 mL of water. The solution was refluxed 19 hr after which it was poured into 100 mL of water and extracted with four 100-mL portions of chloroform. The organic extracts were combined, dried with anhydrous magnesium sulfate, and the solvent removed by rotary evaporator. The residue was chromatographed on deactivated alumina. Elution with ether-ligroin mixtures and 100% ether removed the azo compound. Crystallization from ether gave 1.20 g (31%): nmr (CCl_4) δ 7.10-7.80 (m, 6, aromatic), 6.08 (bs, 2, bridgehead), 2.01 (bs, 4, methylene).

5. 6b,7a-Dihydro-7*H*-cycloprop[*a*]acenaphthylene (124)

This material was prepared by the general method of Kawabata, Naka, and Yamashita[62] for making cyclopropanes from alkenes.

To 50 mL of benzene were added 610 mg (4 mmol) of acenaphthylene, 1.0 mL (39 mmol) of methylene iodide, 1.14 g of copper powder, and 0.05 g of iodine. The mixture was refluxed in air for 46 hr. After cooling, the solid material was removed by filtration, and the

solvent was removed by rotary evaporator. The residue was chromatographed on a 10% silver nitrate-alumina column. Elution with 5% ether-95% ligroin gave 290 mg (44%) cyclopropane: mp 115.0-116.0° C (lit.[58] 115-116° C); nmr (CCl_4) δ 7.14-7.84° C (m, 6, aromatic), 2.89 (dd, 2, J=4.0,8.0 Hz, benzyl), 1.40 (dt, 1, J=4.0,8.0 Hz, exo), 0.71 (dt, 1, J=4.0,4.0 Hz, endo).

6. 1,8-*bis*(Hydroxymethyl)naphthalene (129)

This material was prepared by a modification of the procedure of Mitchell, Topsom, and Vaughan.[82]

A suspension of 100 g (0.50 mol) of naphthalic anhydride in 250 mL of benzene was added over 2 hr to a vigorously stirred suspension of 50 g (1.3 mol) of lithium aluminum hydride in 1 L of anhydrous ether and 200 mL of benzene. The mixture was then refluxed 19 hr. After cooling, the excess hydride was destroyed by the careful addition of water, resulting finally in the precipitation of a gray solid mass. Additional ether was added to the flask, and the solid was collected, washed with ether, and allowed to air dry. This material was then extracted in portions with chloroform by means of a Soxhlet extractor, giving 73.6 g (78%) of white needles: mp 155.0-155.5° C (lit.[82] 158° C).

7. 1,8-*bis*(Bromomethyl)naphthalene (130)

This material was prepared by the procedure of Carpino.[50]

A suspension of 20.0 g (0.11 mol) of 1,8-bis(hydroxymethyl)-naphthalene in 200 mL of methylene chloride was stirred mechanically while 21 mL (0.22 mol) of phosphorus tribromide were added dropwise

over 30 min at room temperature. All of the diol had dissolved by the end of the addition, and stirring was continued an additional 2 hr. Following this, 30 mL of water were added slowly, which caused refluxing and the evolution of gas, and stirring was continued 40 min. Water was added and the organic phase was collected, washed with water, and dried with anhydrous magnesium sulfate. Removal of the solvent by rotary evaporator and recrystallization of the residue from 1:1 benzene-ligroin afforded 20.0 g (60%) of colorless crystals: mp 130.0-131.5° C (lit.[50] 130-131.5° C).

8. 1,4-Dihydronaphtho[1,8-*de*][1,2]diazepine (89)

This material was prepared in a three-step synthesis starting with 1,8-bis(bromomethyl)naphthalene, using a slightly modified version of the procedure of Carpino.[50]

a. *tert*-Butyl-1,2,3,4-tetrahydronaphtho[1,8-*de*][1,2]diazepine-2,3-dicarboxylate (131). To a stirred mixture of 5.37 g of a sodium hydride oil dispersion (57% by weight hydride) in dry dimethylformamide were added 14.8 g (0.064 mol) of t-butyl hydrazodiformate over 30 min. After 30 min of additional stirring, 20.0 g (0.064 mol) of 1,8-bis(bromomethyl)naphthalene was added, and the mixture was stirred 21 hr. Water was added and the mixture was extracted with seven 100-ml portions of ether. The combined ether extracts were dried with anhydrous magnesium sulfate, and removal of the solvent gave a brown oil, which crystallized on standing.

b. 1,2,3,4-Tetrahydronaphtho[1,8-*de*][1,2]diazepine hydrochloride (132). The residue from part a was dissolved in 200 mL of ether and 75 mL of methanol. Dry HCl gas was bubbled through this solution

for 45 min, after which the flask was stoppered and allowed to stand overnight. Decantation of the solvent afforded 4.8 g of crude solid material.

c. 1,4-Dihydronaphtho[1,8-*de*][1,2]diazepine (89). The solid residue from part b was dissolved in 250 mL of hot water and treated with decolorizing carbon. After filtration, 6 g of sodium bicarbonate was added to the solution, which was then extracted with five 60-ml portions of ether. The ether extracts were dried with anhydrous magnesium sulfate, filtered, and then stirred with 9 g of red mercuric oxide for 15 min. The mixture was filtered, and the solvent was allowed to slowly evaporate, giving orange crystals. The total yield of azo compound from the 20.0 g of starting dibromide was 1.65 g (14%): nmr (CCl_4) δ 7.03-7.60 (m, 6, aromatic), 5.63 (s, 4, benzyl).

9. 1,2-Dihydro-1,2-diphenyl-1,2-acenaphthylenediol (134)

This material was prepared by the procedure of Bachmann and Chu.[83]

Phenylmagnesium bromide was prepared by the addition of 30.0 mL (0.28 mol) of bromobenzene to 9.0 g (0.38 mol) of magnesium turnings in 300 mL of anhydrous ether. After the solution was refluxed 1 hr, 18.2 g (0.10 mol) of acenaphthenequinone were added in portions over 30 min. The solution was refluxed 3 hr and then allowed to stir at room temperature 18 hr. The mixture was poured into 800 mL of ice containing 30 mL of glacial acetic acid. This solution was then extracted with ether, which was washed with water and aqueous sodium carbonate. After the organic phase was dried with anhydrous magnesium sulfate, the ether was removed by rotary evaporator. The residue was

crystallized from ethanol-water-acetone to give 23.3 g (69%) of pale yellow needles, which were used without further purification.

10. 1,2-Diphenylacenaphthylene (126)

This material was prepared by a modification of the procedure of Richter and Feist.[63]

A suspension of 1.00 g (3.0 mmol) of 1,2-dihydro-1,2-diphenyl-1,2-acenaphthylenediol in 75 mL of 57% aqueous hydriodic acid was heated on a steam bath 1 hr, during which the suspended material became deep orange. The mixture was filtered through glass wool, and the solid collected was dissolved in chloroform and washed with water and aqueous sodium carbonate. After drying with anhydrous magnesium sulfate, the solvent was removed by rotary evaporator. The residue was chromatographed on alumina, eluting with 5% ether-95% ligroin. This afforded 0.51 g (57%) of orange material which was crystallized from acetone-water to give orange needles: mp 161.0-162.0° C (Chu.[83] 161.3° C).

11. *cis*-1,2-Dihydro-1,2-diphenylacenaphthylene (135)

This material was prepared by the procedure of Richter and Feist.[63]

A suspension of 133 mg (0.44 mmol) of 1,2-diphenylacenaphthylene and 75 mg of 5% palladium on powdered charcoal in 200 mL of absolute ethanol was shaken 48 hr under a hydrogen atmosphere on a Parr hydrogenation apparatus. At the end of this time the orange color of the original mixture had completely disappeared. Filtration of the mixture and removal of the solvent by rotary evaporator gave 119 mg

(89%) of white flakes, which were recrystallized from 95% ethanol to afford white needles: mp 146.0–146.5° C (lit.[63] 146–147° C); nmr ($CDCl_3$) δ 6.40–7.73 (m, 16, aromatic), 5.17 (s, 2, benzyl); uv (95% ethanol) 291 nm (ε = 8810).

12. *trans*-1,2-Dihydro-1,2-diphenylacenaphthylene (136)

This material was prepared by the procedure of Bauld and Hudson.[53]

A solution of sodium ethoxide in ethanol was prepared by dissolving sodium wire in 100 mL of absolute ethanol. After the sodium was no longer visible, 400 mg (1.3 mmol) of cis-1,2-dihydro-1,2-diphenylacenaphthylene was added to the solution, which was refluxed under nitrogen overnight. Water was added, and the mixture was extracted with ether. After drying with anhydrous magnesium sulfate, the ether was removed by rotary evaporator. The residual oil was chromatographed on silica gel, eluting with 2% ether–98% ligroin. The yellow oil obtained would not crystallize; but since the nmr spectrum showed essentially pure material, it was used without further purification: nmr ($CDCl_3$) δ 6.03–7.74 (m, 16, aromatic), 4.73 (s, 2, benzyl).

13. 1*H*,4*H*-1,4-Ethenonaphtho[1,8-*de*][1,2]dioxepin (168)

A solution of 340 mg (1.9 mmol) of cyclohepta[de]naphthalene and 23 mg of meso-tetraphenylporphine in 5.5 mL of methylene chloride was photolyzed at -78° C by a Hanovia medium-pressure mercury vapor lamp while oxygen was bubbled through the solution. After 2 hr of irradiation, the solvent was removed by rotary evaporator, and the solid was dissolved in methanol. Filtration removed most of the

sparingly soluble sensitizer. The solvent was then removed, and the residue was chromatographed on silica gel. Elution with 5% ether-95% ligroin removed unreacted cyclohepta[de]naphthalene while 10% ether-90% ligroin eluted the remaining sensitizer. Elution with 20% ether-80% ligroin afforded 273 mg (68%) of white flakes: mp 134.5-135.5° C; nmr ($CDCl_3$) δ 7.07-7.90 (m, 6, aromatic), 6.65 (dd, 2, J=3.2,5.2 Hz, vinyl), 5.46 (dd, 2, J=3.2,5.2 Hz, bridgehead); uv (95% ethanol) 294 nm (ε = 5400); mass spectrum (70 eV) [m/e (relative intensity)] 210 (4.3), 178 (100), 152 (43).

Anal. Calcd. for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 78.42; H, 4.85.

14. 1*H*,4*H*-1,4-Ethanonaphtho[1,8-*de*][1,2]dioxepin (158)

This material was prepared by the general procedure of Adam and Eggelte[72] for the reduction of unsaturated peroxides.

To a solution of 160 mg (0.76 mmol) of 1H,4H-1,4-ethenonaphtho[1,8-de][1,2]dioxepin in 20 mL of methylene chloride (distilled from calcium hydride) was added 3.3 g of dipotassium azodicarboxylate.[84] While stirring under nitrogen, the mixture was cooled to -78° C; and a solution of 2 mL of glacial acetic acid diluted to 10 mL with methylene chloride was added dropwise. Following the addition, the mixture was returned slowly to room temperature and left to stir overnight. The solids present were filtered from the mixture, and the solvent was removed by rotary evaporator. The residue was chromatographed on silica gel, eluting with 6% ether-94% ligroin. The oil obtained was crystallized from ligroin giving white needles: mp

88.0-89.0° C; nmr ($CDCl_3$) δ 7.18-7.88 (m, 6, aromatic), 5.29-5.40 (m, 2, bridgehead), 2.41-2.85 (m, 2, methylene), 1.92-2.15 (m, 2, methylene); uv (95% ethanol) 286 nm (ε = 6900); mass spectrum (25 eV) [m/e (relative intensity)] 212 (83), 180 (48), 165 (100).

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.22; H, 5.90.

15. Attempted Synthesis of 1*H*,4*H*-Naphtho[1,8-*de*][1,2]dioxepin (176)

This synthesis employs the general procedure of Johnson and Nidy[76] for the preparation of dialkyl peroxides.

To a small flask containing 30 mL of benzene (fresh) was added 2.02 g (28.5 mmol) of potassium superoxide, which was crushed to a fine powder. 1,8-bis(Bromomethyl)naphthalene (2.17 g, 6.9 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6, 150 mg) were added, and the mixture was stirred at room temperature under nitrogen overnight. This was then poured into 100 mL of aqueous sodium chloride. The organic phase was collected and dried with anhydrous magnesium sulfate, and the benzene was removed by rotary evaporator. The residue was chromatographed on silica gel, eluting with 20% ether-80% ligroin. The yellow oil obtained was sublimed, giving a white powdery material: mass spectrum (25 eV) [m/e (relative intensity)] 170 (100), 142 (47), 141 (56).

16. Attempted Synthesis of 1,4-Dihydro-1,4-ethanonaphtho[1,8-*de*][1,2]diazepine-2,3-dioxide (181)

This synthesis employs the general procedure of Snyder, Heyman, and Suciu[79] for the preparation of azo dioxides.

To a small flask containing 100 mg (0.5 mmol) of 1,4-dihydro-1,4-ethanonaphtho[1,8-de][1,2]diazepine were added 10 mL of glacial acetic acid and 10 mL of 30% hydrogen peroxide. The solution was stirred under nitrogen at room temperature overnight. The excess peroxide was then destroyed by the dropwise addition of a saturated aqueous solution of sodium bisulfite. The solution was poured into 200 mL of water, and solid sodium carbonate was added in portions until no more fizzing occurred and the solution was basic to pH paper. The product was extracted into methylene chloride. After drying with anhydrous magnesium sulfate, the solvent was removed by rotary evaporator, giving an orange oil: nmr ($CDCl_3$) δ 7.10-7.85 (m, 6, aromatic), 5.57 (bs, 1, bridgehead), 5.30 (bs, 1, bridgehead), 2.13-2.57 (m, 4, methylene); mass spectrum (25 eV) [m/e relative intensity)] 224 (38), 194 (100).

17. 6b,7a-Dihydro-7*H*-cycloprop[*a*]acenaphthylene-*6b,7a*-d_2 (152)

This material, prepared from acenaphthylene-1,2-d_2, was provided by R. M. Pagni.

18. (1α,4α,11*R**,12*S**)-1,4-Dihydro-1,4-ethanonaphtho[1,8-*de*][1,2]diazepine-*11,12*-d_2 (171)

This material was prepared in an identical manner to the non-deuteriated azo compound 103, starting from 2,3-dihydro-1,2,3-metheno-1H-phenalene-2,10-d_2 provided by R. M. Pagni.

C. Photolyses

The light source for all photolyses was a medium-pressure mercury vapor Hanovia lamp.

Samples to be photolyzed at room temperature without light filtration were fastened directly to the cooling jacket of the lamp. Samples requiring light filtration were placed inside a box lined with aluminum foil with a small window covered with Corning colored filter #3060 ($\lambda \geq 380$ nm).

Degassed samples were photolyzed in nmr tubes which had been sealed after three "freeze-pump-thaw" cycles. Solutions of samples to be photolyzed in the presence of oxygen or nitric oxide were placed in test tubes into which the desired gas was bubbled directly from its cylinder. Nitric oxide photolyses were conducted in the hood.

Low temperature photolyses were conducted by placing the sample tube in a glass Dewar flask containing dry ice-acetone and placing this entire assembly next to the lamp.

When controls were to be run, a sample tube identical to the one being photolyzed was wrapped in aluminum foil and placed next to it during the photolysis.

D. Thermolyses

Most thermolyses were conducted in an oil bath thermostatted at the desired temperature. The thermolyses of cis- and trans-1,2-dihydro-1,2-diphenylacenaphthylene were conducted using the flame of a Bunsen burner as the heat source.

Degassed samples were thermalized in nmr tubes which had been sealed after three "freeze-pump-thaw" cycles. Solutions of samples to be thermalized in the presence of oxygen or nitric oxide were placed in test tubes into which the desired gas was bubbled directly from its cylinder. Nitric oxide thermolyses were conducted in the hood.

E. Kinetics

A solution of 6b,7a-dihydro-7H-cycloprop[a]acenaphthylene was prepared in benzene-d_6 containing a small amount of TMS to be used as an internal standard. The solution was divided into three nmr tubes which were degassed by three "freeze-pump-thaw" cycles and sealed. The nmr spectrum of the first tube was recorded, and the tube was placed in an oil bath thermostatted at 140 ± 1° C. At the end of the required time interval, the tube was rapidly removed from the oil bath and plunged into ice water. The nmr spectrum was then recorded, monitoring the disappearance of the cyclopropane relative to the internal TMS standard. The procedure was repeated until the sample had been thermalized for a total of 12 hr. The thermolyses of the other two tubes were conducted at 155 ± 1° C for a total of 4.5 hr and at 170 ± 1° C for a total of 4 hr, respectively. The data were analyzed by the least squares computer program given in The Chemist's Companion,[85] modified to calculate error limits and activation parameters.

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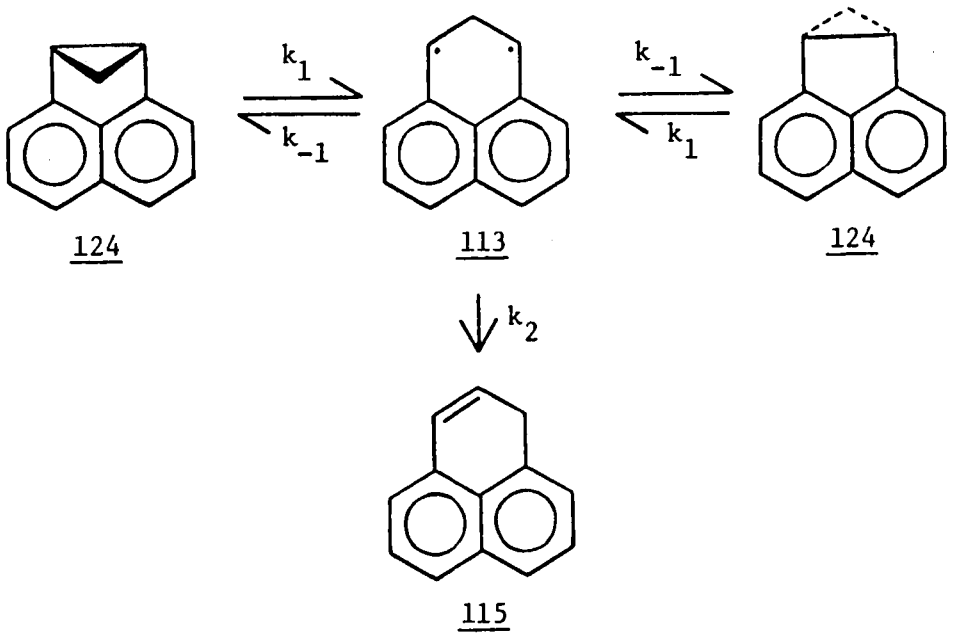
APPENDIX

APPENDIX

KINETICS OF 6b,7a-DIHYDRO-7H-CYCLOPROP[a]ACENAPHTHYLENE

A. Complete Scheme



In the equations below, the cyclopropane 124 will be represented by the letter C and the intermediate 113 by the letter I.

The disappearance of C with time is given by the following expression.

$$-\frac{d[C]}{dt} = 2k_1[C] - 2k_{-1}[I] \qquad \text{(A-1)}$$

This equation can be made independent of [I] if the steady-state approximation is made.

$$\frac{d[I]}{dt} = 0 = 2k_1[C] - 2k_{-1}[I] - k_2[I] \qquad \text{(A-2)}$$

$$(2k_{-1} + k_2)[I] = 2k_1[C] \qquad \text{(A-3)}$$

$$[I] = \frac{2k_1}{2k_{-1} + k_2}[C] \qquad \text{(A-4)}$$

Substitution of this value for [I] into Equation A-1 gives the following.

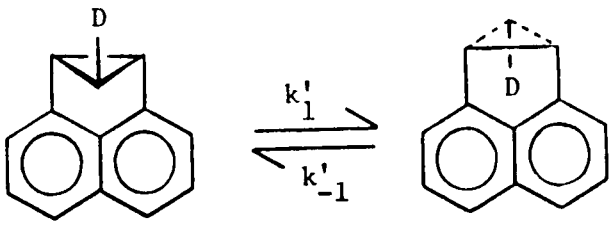
$$-\frac{d[C]}{dt} = 2k_1[C] - 2k_{-1}\left(\frac{2k_1}{2k_{-1} + k_2}\right)[C] \qquad \text{(A-5)}$$

$$-\frac{d[C]}{dt} = 2k_1[C] - \frac{4k_{-1}k_1}{2k_{-1} + k_2}[C] \qquad \text{(A-6)}$$

$$-\frac{d[C]}{dt} = \frac{4k_{-1}k_1 + 2k_1k_2 - 4k_{-1}k_1}{2k_{-1} + k_2}[C] \qquad \text{(A-7)}$$

$$-\frac{d[C]}{dt} = \frac{2k_1k_2}{2k_{-1} + k_2}[C] \qquad \text{(A-8)}$$

B. Epimerization Without Intermediate



91 93

In the equations below, the exo-deuteriocyclopropane 91 will be represented by the letter X and the endo-deuteriocyclopropane 93 by the letter N.

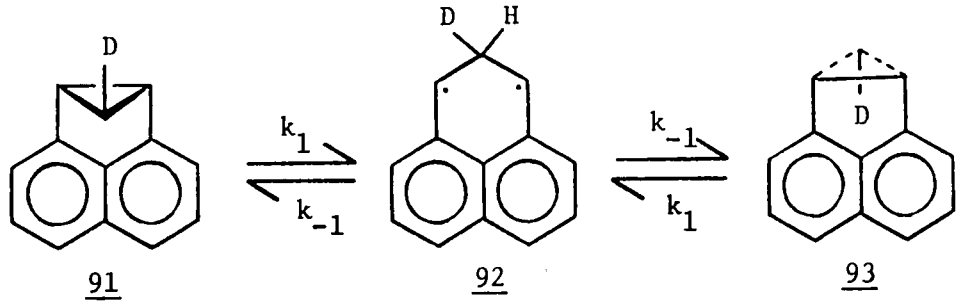
The disappearance of X with time is given by the following expression.

$$-\frac{d[X]}{dt} = k'_1[X] - k'_{-1}[N] \qquad \text{(A-9)}$$

Assume $k'_1 \approx k'_{-1}$.

$$-\frac{d[X]}{dt} = k'_1[X] - k'_1[N] \qquad \text{(A-10)}$$

C. Epimerization With Intermediate



91 92 93

In the equations below, the exo-deuteriocyclopropane 91 will be represented by the letter X, the endo-deuteriocyclopropane 93 by the letter N, and the intermediate 92 by the letter I.

The disappearance of X with time is given by the following expression.

$$-\frac{d[X]}{dt} = k_1[X] - k_{-1}[I] \qquad \text{(A-11)}$$

This equation can be made independent of [I] if the steady-state approximation is made.

$$\frac{d[I]}{dt} = 0 = k_1[X] - 2k_{-1}[I] + k_1[N] \qquad \text{(A-12)}$$

$$2k_{-1}[I] = k_1[X] + k_1[N] \qquad \text{(A-13)}$$

$$[I] = (k_1/2k_{-1})[X] + (k_1/2k_{-1})[N] \qquad \text{(A-14)}$$

Substitution of the value for [I] into Equation A-11 gives the following.

$$-\frac{d[X]}{dt} = k_1[X] - k_{-1}\{(k_1/2k_{-1})[X] + (k_1/2k_{-1})[N]\} \qquad \text{(A-15)}$$

$$-\frac{d[X]}{dt} = k_1[X] - \frac{k_1}{2}[X] - \frac{k_1}{2}[N] \qquad \text{(A-16)}$$

$$-\frac{d[X]}{dt} = \frac{k_1}{2}[X] - \frac{k_1}{2}[N] \qquad \text{(A-17)}$$

Comparison of Equations A-10 and A-17 gives the following correlation.

$$\frac{k_1}{2} = k_1' \qquad \text{(A-18)}$$

$$k_1 = 2k_1' \qquad \text{(A-19)}$$

VITA

Michael Neal Burnett was born in Knoxville, Tennessee on December 4, 1951. He attended schools in that city and graduated as valedictorian of Halls High School in June 1969. He immediately entered The University of Tennessee, and in June 1973 he received a Bachelor of Science in Chemistry degree, graduating "With Highest Honors." In September 1973 he entered the Graduate School at The University of Tennessee and held a graduate teaching assistantship in the Department of Chemistry until June 1976. He was the recipient of a teaching award, three National Alumni Association Graduate Scholarships, and a University of Tennessee Non-Service Fellowship. The author is a member of the American Chemical Society, Sigma Xi, Phi Kappa Phi, and Phi Beta Kappa.