Generation and Characterization of a Bridged 1,8-Naphthoquinodimethane[1]

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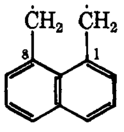
Abstract: Reported is the preparation and characterization of the bridged 1,8-naphthoquinodimethane (**2**). The synthesis of **2** depended on a high yield preparation of pleiadiene (**3**). Attempts to initiate this preparation of **3** via the reaction of phenalenone (**4**) with dimethyloxosulfonium methylide were unsuccessful. Reaction of the phenalenyl anion (**11**) with methylene chloride and *n*-butyllithium did afford **3** as a minor product in addition to the major product, the bicyclobutane **12**. Several methods were found for converting **12** into **3**. The azo compound **16a**, the immediate precursor to **2**, was prepared from pleiadiene (**3**) in a series of logical steps. Both pyrolysis and photolysis of **16a** in a variety of solvents afforded naphthocyclobutane (**17a**, major product) and 1,8-divinylnaphthalene (**18a**, minor product). No other products were formed. The relative percentages of **18a** and **17a** were not altered when the singlet-triplet perturbing agents, air, iodobenzene, and hexafluorobenzene, were added. Attempts to trap **2** with three olefins were unsuccessful. Both pyrolysis and photolysis of **16b**, a sterospecifically deuterium-labeled precursor to **2**, yielded **17** and **18** with a "random" distribution of deuterium. This not only demonstrates the existence of **2** but also says something about the dynamic behavior of **2**. Irradiation of **16a** in hexafluorobenzene inside the probe of an ESR spectrometer at liquid nitrogen temperature afforded the triplet of **2**, and it lies 200 cal/mol above the ground state. **2** underwent an irreversible decay at −130 °C to a radical species (not characterized) as well as to **17** and **18**. Irradiation of **16a** in an ethanol glass at liquid nitrogen temperature also afforded the triplet. A preparative photolysis of **16a** in ethanol at liquid nitrogen temperature afforded **18** (and **17**). This demonstrated that triplet **2**, at least in part, is an intermediate in the conversion of **16a** into **17** and **18**. Irradiation of **16b** under these conditions gave **17** and **18** with the same deuterium distribution as was observed in fluid solution. A coherent mechanism is presented that explains all the known facts about the conversion of **16** into **17** and **18**.

Introduction

There has been a large amount of activity in recent years devoted to the preparation of organic molecules having triplet ground states. The impetus for this activity has been based on the remarkable predictive power of Hückel MO theory in this regard. For example, triplet ground states have been observed for the cyclopentadienyl cation,[3] trimethylenemethane,[4] tetramethyleneethane,[5] and a derivative of *m*-xylylene[6] in complete agreement with the Hückel prediction.

There are numerous other organic molecules which are predicted to have triplet ground states. A particularly interesting molecule in this category is the 1,8-naphthoquinodimethane (**1**). As is usually the case, the prediction of a triplet ground state for **1** is based on a totally planar structure. This does not seem like a reasonable assumption here because of the close proximity of the methylenes (peri interaction) attached to C-1 and C-8. Because of this close proximity, in addition to the deviation of these sites from planarity, there may also be a direct electronic interaction (overlap) between the nonbonded orbitals on these methylenes. In other words, because of steric and electronic effects, the Hückel prediction for **1** may be based on an inadequate model. It is an interesting question then whether this entity will have a triplet ground state and, if not, whether one can attribute this fact to thse steric and electronic factors.



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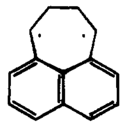

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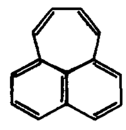

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There are several reports in the literature where **1**[7] or a derivative of **1**[8,9] is likely an intermediate in a chemical reaction, but in none of these reactions has the existence of the reactive intermediate been demonstrated, let alone characterized. For these reasons, the 1,8-naphthoquinodimethane system seemed worthy of study. Although **1** itself was likely available,[7] because of its synthetic accessibility and possible stereochemical studies available to it, the bridged 1,8-naphthoquinodimethane (**2**) was chosen for investigation.

Preparation of Pleiadiene (3)

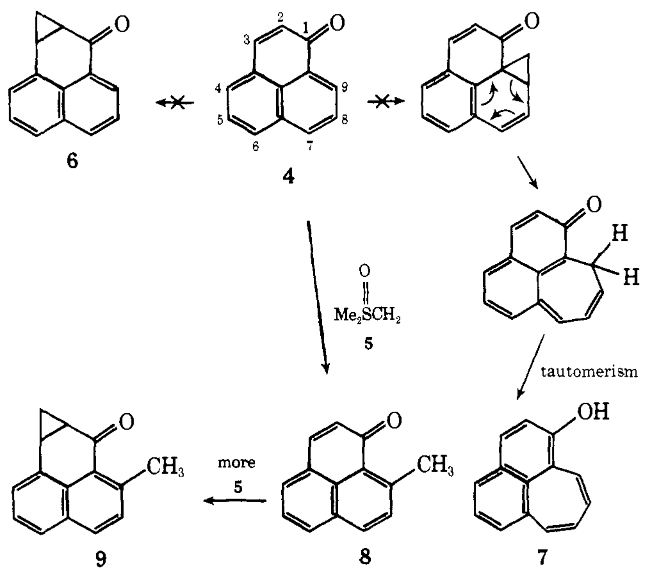
The preparation of the bridged quinodimethane (**2**) depended on the availability of a high-yield synthesis of pleiadiene (**3**) (or a derivative), a hydrocarbon having the same carbon skeleton as **2**. Boekelheide[10] and Meinwald[11] have both previously reported preparations of **3**, but these seemed inadequate for our purposes. Our attention thus was directed elsewhere.

Our first approach to the preparation of the pleiadiene ring system was based on the anticipated reaction between phenalenone (**4**)[12] and dimethyloxosulfonium methylide (**5**)[13] (Scheme I). Reaction between these two species might be expected to give either cyclopropaphenalenone (**6**), a ketone which could possibly be converted into **3**, or 1-hydroxypleiadiene (**7**). This latter prediction is based on the propensity of **4** to react with nucleophiles such as hydrides[14] and Grignard reagents[15] at C-9. The prediction of the attack of the methylide at C-9 was observed; unfortunately, 9-methylphenalenone (**8**) was formed instead of **6** or **7**.[1d]

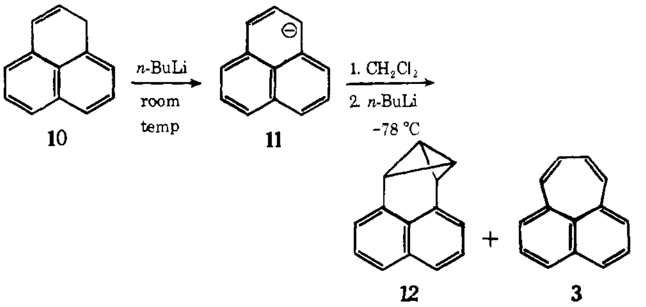
Our successful preparation of **3** was based on the procedure used by Katz in the synthesis of benzvalene.[16] Treatment of an ether solution of phenalene (**10**),[14] first with *n*-butyllithium at room temperature and then with methylene chloride and *n*-butyllithium at dry ice-acetone temperature, afforded a mixture of two products,[1a,17] the minor one of which was **3**. The major product could be separated from **3** by repeated crystallization from ligroine and was identified as the bicyclobutane (**12**). The two products, **3** and **12**, were formed in a ratio of 1:5 and an overall yield of 68%.

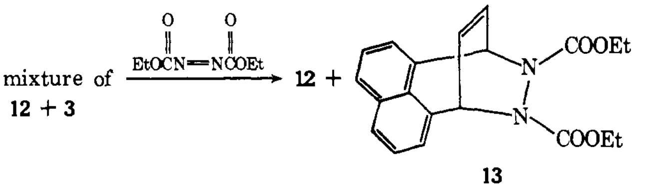
To study the chemical behavior of **12**, it was impractical to separate it from **3** by the crystallization procedure. Heating the mixture of **12** and **3** in CCl_4 at 75 °C with excess

Scheme I

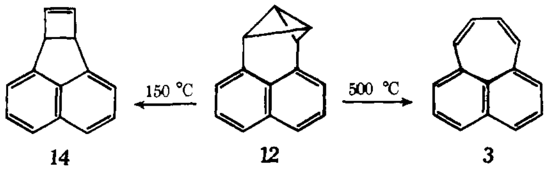


ethyl azodicarboxylate afforded a product mixture which was easily separated by column chromatography. The products were identified as unreacted **12**, ethyl azodicarboxylate, and the Diels–Alder adduct **13**. Control experiments demonstrated that **12** was inert under the reaction conditions. It may seem surprising at first that **12** is inert to reaction with ethyl azodicarboxylate, but the reaction must be initiated on the underside of the bicyclobutane,[18] and this is inhibited by the presence of the naphthalene skeleton. This effect is so dominant that **12** did not react even with *N*-phenyltriazolinedione in CH_3CN after 19 h at room temperature.



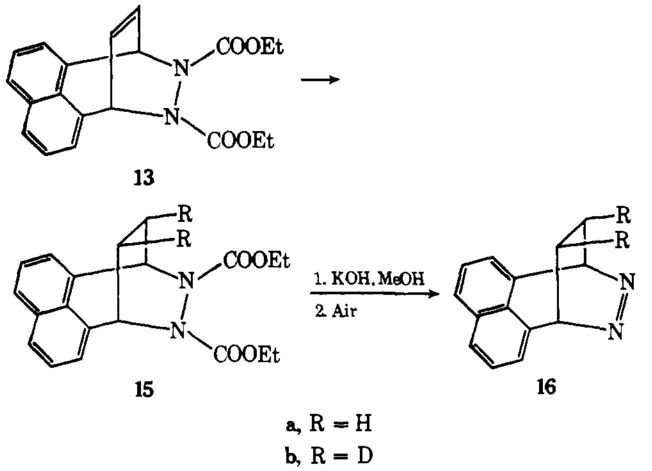


Our primary interest, of course, was in preparing **3**. Clearly, it was necessary to find a viable procedure for the conversion of **12** into pleiadiene. As it turns out, there are several acceptable methods for doing this. Heating a cyclohexane solution of **12** at 150 °C smoothly converted it into **14**,[19] which is known to isomerize to pleiadiene at higher temperatures.[11] Indeed, when a solution of **12** in hexane was passed through a hot tube (500 °C), it was converted into **3**. For preparative purpose, it was not necessary to separate **3** and **12**; the mixture could be pyrolyzed at 500 °C in the hot tube. Under these conditions **12** is converted into **3**, and **3** passes through the tube unscathed. Other methods which converted **12** into **3** were irradiation of **12** at 2537 Å, treatment with $AgClO_4$ in benzene,[17] and treatment with a catalytic amount of iodine in CCl_4. The yields of the transformation were all in the range of 60 to 80%. The iodine procedure is a particularly good one, though, because the reaction is rapid at room temperature and product isolation is very simple.



Preparation of Azo Compound (16)

The next objective of the syntheses was the preparation of the bicyclo azo compound **16**, the immediate precursor of **2**. The first step involved the Diels–Alder reaction of pleiadiene with ethyl azodicarboxylate as described in the previous section. Hydrogenation of the resulting viscous oil (**13**), followed by saponification with KOH in methanol and exposure to air, afforded **16a**. Although many cyclic azo compounds are unstable, no difficulties were experienced in handling **16a**; it was perfectly stable at room temperature in the absence of light.



For stereochemical studies to be described later, **13** was also reduced with diimide-d_2. It was not possible to decide on which side of the double bond of **13** the diimide-d_2 had attacked by comparing the NMR's of **15a** with **15b**. When **15b** was converted to **16b**, even here the assignment could not be made by comparing the NMR's of **16a** and **16b**, because the chemical shifts of the syn and anti hydrogens of **16a** are superimposable. However, comparison of the NMR's of these two substances in the presence of the shift reagent $Eu(fod)_3$-d_{30} revealed that the deuteriums were predominantly on the nitrogen side of **16**, i.e., deuterated **16** was **16b**. Working backwards, it is obvious that diimide-d_2 had attacked **13** from the nitrogen side of the molecule.

Assignment of hydrogens with the aid of shift reagents can be tricky, because there is an angular dependence as well as a distance dependence on the magnitude of the shift of a hydrogen in relationship to the site of complexation. In the present case, even if the assignments are wrong and should be reversed, as will be seen later, it will not affect the conclusion drawn from these studies.

Thermal and Photochemical Decomposition of 16

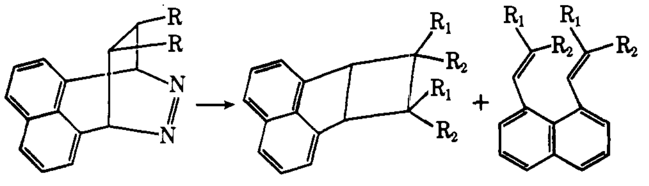
Although **16a** was perfectly stable at room temperature, heating a degassed $CCl_2{=}CCl_2$ solution at 134 °C resulted in its complete disappearance. The decomposition was found to obey first-order kinetics ($\Delta H^{\ddagger} = 27.5 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -6.7 \pm 0.6$ cal/K mol) and result in the

Table I. Product and Deuterium Distribution[a,b]

Reactant	Solvent[c]	Relative percentages (**18**:**17**) and decomposition conditions: Δ,[d] 134 °C	hν,[e] 20 °C	hν,[e] (temp)	Deuterium ratio: **17b**: **17c**	**18b**: **18c**
16a	CH_3OH	11:89	13:87	<2:>98 (−77 °C)[f,g]		
16a	CH_2Cl_2			<2:>98 (−77 °C)[f,g]		
16a	CH_3CH_2OH			100:0 (−196 °C)[f,h]		
16a	CCl_2CCl_2	12:88	19:81			
16a	Cyclohexane	13:87				
16a	Benzene	18:82	10:90			
16a	CCl_4	12:88	14:86			
16b	CCl_4	13:87			1	1
16b	CCl_4		15:85		1	1
16b	CH_3CH_2OH			71:29 (−196 °C)[f]	1	1
16a	1-Chloronaphthalene	17:83[i,j]				
16a	Hexafluorobenzene	12:88	11:89			
16a	Ethyl iodide	[k]	[k]			
16a	Iodobenzene	15:85	20:80			

[a] All product and deuterium ratios were determined by ^1H NMR, usually on the original reaction mixture. In a few cases, because of peak overlap, solvent was removed before analysis. [b] Controls were run to demonstrate that the product and deuterium ratios were the initial ones. [c] Samples were prepared by the freeze-pump-thaw procedure, unless otherwise stated. [d] Thermal decomposition. [e] Photochemical decomposition at 3500 Å. [f] Decomposition run under deoxygenated nitrogen. [g] **18** was barely detectable. [h] **17** could not be detected. [i] Run in air in the heated probe of an NMR spectrometer. [j] Reaction temperature of 140 °C. [k] Ethyl iodide was unstable under the reaction conditions.

formation of two products. These two compounds were separated on a silver nitrate impregnated alumina column and identified as naphthocyclobutane (**17a**) and 1,8-divinylnaphthalene (**18a**)[20] by independent synthesis in each case.



16a, R = H
b, R = D

17

18

a, $R_1 = R_2 = H$
b, $R_1 = D$; $R_2 = H$
c, $R_1 = H$; $R_2 = D$

Careful scrutiny of the reaction product NMR and the chromatography revealed the presence of no other products.

The thermal decomposition of **16a** could be accomplished in a wide variety of other solvents (Table I). As in $CCl_2{=}CCl_2$ solution, only **17a** and **18a** were observed as products, with **17a**, in all cases, the major product.[21] Furthermore, in those cases which were checked, the overall yield of the two products was close to 100%. The relative percents of **18a** and **17a** reported in Table I were shown to be the initial ones, because **17a** and **18a** did not interconvert or yield other compounds under the reaction conditions.[22,23] In addition, the thermolysis of **16a** in 1-chloronaphthalene was run in the heated probe (140 °C) of an NMR spectrometer; the ratio **18a**:**17a** in this case was invariant as a function of time.

Similar results were obtained on irradiating **16a** with 3500 Å light at room temperature. Control experiments again demonstrated the stability of both **17a** and **18a** under the reaction conditions. As in the thermal decompositions, no other products were observed in any of the solvents investigated. Although the percentage of **18a** was approximately 15 at room temperature, when the photochemical reaction was run in methanol and methylene chloride at −77 °C, as might be expected, the percent approached 0, i.e., the yield of **18a** became quite low. Quite remarkably, when the photolysis was run at an even lower temperature (77 K) in an ethanol glass, the predominant product became 1,8-napthalene. There is clearly a difference in behavior in the decomposition of **16a** in fluid and rigid solution.

If **2** is an intermediate in these decompositions, depending on its intrinsic lifetime, one might expect to find as a product of the decomposition: dimers of **2**, adducts derived from solvent addition to **2**, and/or adducts derived from hydrogen or chlorine abstraction by **2** from the solvent. As already mentioned, none of these compounds was ever observed. In fact, even when the trapping agents, dimethyl maleate, dimethyl fumarate, and tetracyanoethylene, were added to reaction solutions, no adducts were observed. These facts attest to the short-lived nature of **2**, if indeed it is an intermediate in the reaction.

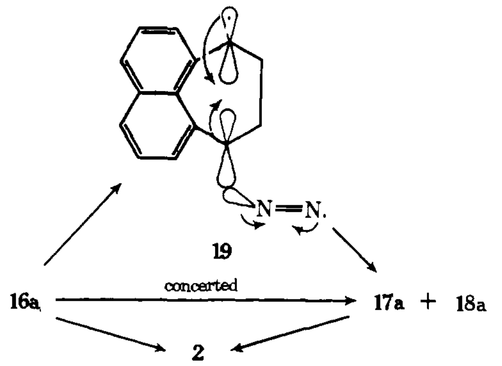
Because **2** can exist possibly in both a singlet and triplet electronic state, one would expect that when the azo decompositions are run in the presence of chemicals that increase the rate of singlet-triplet interconversion, the product distribution would change. Although there are several possible ramifications of this singlet-triplet interconversion, one might imagine, as a possibility, that the decompositions proceed totally along a singlet energy surface in normal solvents. In the presence of these perturbing agents, however, singlet **2** is converted to triplet **2** and, because of its long lifetime, it dimerizes.

To see if the product distribution could be altered, **16a** was pyrolyzed in 1-chloronaphthalene in the presence of air and decomposed both thermally and photochemically in degassed iodobenzene and hexafluorobenzene. There was no difference in the product distribution in any of these cases when compared with normal solvents. Clearly, the reaction pathway must be the same in these solvents as in the others. For whatever reason, **2** is not being affected by these reagents.

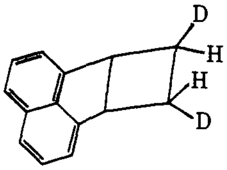
Perhaps the easiest explanation for the imperturbability of the system is that **2** is not an intermediate in the decomposition of **16a**. Perhaps the decomposition of **16a** is a totally concerted process or involves intermediates other than **2**

(Scheme II). If either of these processes occurred, one would expect the reactions to be highly stereospecific; whereas, if **2** is intermediate in the reaction, the overall reaction probably would not. To investigate this very important point, we looked at the decomposition of **16b**.

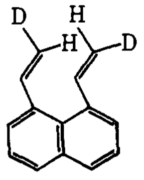
Scheme II



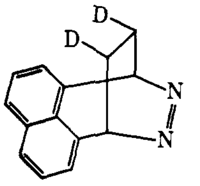
Thermal decomposition of **16b** in CCl$_4$ at 134 °C afforded a mixture of deuterated **17** and **18** in a similar distribution to that observed in the decomposition of **16a**. Analysis of the product mixture revealed that deuterated **17** consisted of a 50:50 mixture of *anti,cis*-dideuterionaphthocyclobutane (**17b**) and *syn,cis*-dideuterionaphthocyclobutane (**17c**). Although it is an unlikely product in any case, no *trans*-dideuterionaphthocyclobutane (**17d**) was observed. The assignments were based on the analysis of the NMR's of **17a** and independently synthesized **17b**. Analysis of deuterated 1,8-divinylnaphthalene product revealed that the label in this case was equally distributed between the two sites on the terminal methylenes, i.e., a 50:50 mixture of cis and trans label. Because there is no spin-spin coupling between the adjacent vinyl groups, the NMR analysis could not distinguish between a 50:50 mixture of *trans,trans*-dideuterio-1,8-divinylnaphthalene (**18b**) and *cis,cis*-dideuterio-1,8-divinylnaphthalene (**18c**) from 100% of the *cis,-trans*-dideuterio-1,8-divinylnaphthalene (**18d**).



17d



18d



16c

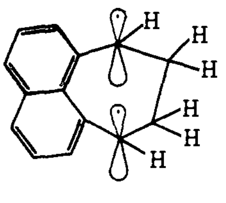
Control experiments on independently prepared **17b** demonstrated that there was no scrambling of label under the reaction conditions. Although a stereospecifically labeled **18** was not available to us, Nelsen has shown[8e] that pyrolysis of **18b** at 350 °C afforded recovered 1,8-divinylnaphthalene which contained only 10% cis label. It seems reasonable that very little isomerization would occur at the much lower temperature used in our studies. Furthermore, checking the ratio of cis and trans label in **18**, as early in the reaction as possible, revealed that it had not changed. In conclusion, the deuterium label in both **17** and **18** reported in Table I is real and does not represent any degradation or isomerization of the initially formed products.

Irradiation of **16b** in degassed CCl$_4$ at 20 °C using 3500 Å light afforded both **17** and **18** with the same distribution of deuterium as was observed in the thermal decomposition. Control experiments again revealed the stability of **17b** under the reaction conditions. Unfortunately, lacking either **18b** or **18c**, we were unable to check the stability of **18** under these conditions. In line with the other controls mentioned above and because **18** does not absorb much light at 3500 Å, it is reasonable to believe that the deuterium distribution in **18** in this case is also the initial one.

There is one additional point of interest concerning these data. Recall that the assignment of the label in **16** was not totally unambiguous. Although **16b**, where the cis deuteriums are on the nitrogen side of the molecule, was the reasonable choice, one could not totally exclude the other possible isomer **16c**, where the cis deuteriums are on the naphthalene side of the molecule, as the actual structure. Had the reaction been highly stereospecific, this would have been a worry. Because of the "randomness" of the label in both products, however, both **16b** and **16c** would be expected to give identical results.

Irradiation of **16a** in an ethanol glass at 77 K had given predominantly **18a**. It was obviously important to look at the deuterium distribution for the photochemical decomposition of **16b** in ethanol glass. Remarkably, both products were formed (**18**, major product), and the deuterium distribution in each product was identical with that observed in fluid solution.

What conclusions can be drawn from these stereochemical studies? First of all, the results demonstrate in an unequivocal manner the existence of **2** as an intermediate in these reactions. It is virtually impossible to explain the pattern of label in **17** and **18** had the reaction proceeded concertedly or through a nitrogen biradical such as **19**.[24] Secondly, the results tell us something about the dynamic behavior of **2**. One can accommodate the deuterium distribition if **2** is either planar, **20** (C_{2v} symmetry), skew or twist, **21** (C_i), or an equilibrating mixture of bent conformers, **22** (C_s), or perhaps some combination of these three. Which of these possibilities is most reasonable will be discussed later.



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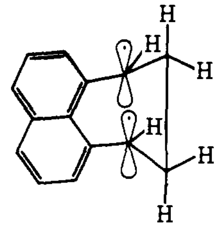

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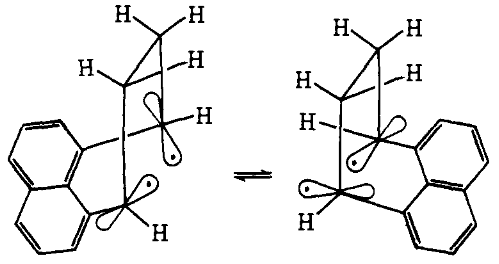

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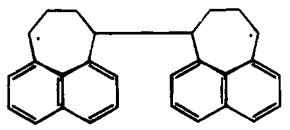
ESR and CIDNP Studies

Although the existence of **2** and something of its dynamic behavior in solution had now been demonstrated, the question of whether the quinodimethane had a triplet ground state remained to be answered. It was hoped that the combined use of CIDNP and ESR would aid in answering this question.

Unfortunately, our attempts to observe a CIDNP in the thermal decomposition of **16a** in the heated probe of an NMR spectrometer were unsuccessful.[26] No conclusions concerning the electronic state of **2** can be made from these experiments. Fortunately, the ESR experiments which we performed were most successful.

Irradiation of a 0.15 M solution of **16a** in hexafluorobenzene at −160 °C inside an optical transmission ESR cavity afforded an ESR spectrum after several minutes. The spectrum exhibited resonance lines characteristic[27] of a randomly oriented triplet species and, in addition, a stronger resonance near $g = 2$, which is attributable to a radical specie(s) (Figure 1). With 9.221 GHz microwave radiation, resonance lines were observed at 3088 and 3480 G and at 3192 and 3375 G and were assigned, respectively, to the signals of a randomly oriented triplet state of **2** oriented perpendicular and parallel to the magnetic field and having an axially symmetric or nearly axially symmetric spin distribution. The $\Delta M_S = \pm 2$ transition for the triplet was very weak but could be observed under high gain and modulation at 1640 G. The zero-field splitting parameters for **2** are $|D| = 0.018\ \text{cm}^{-1}$ and $|E| < 0.003\ \text{cm}^{-1}$. In the case of the latter, the fact that only four triplet resonances appeared in the high-field portion of the triplet spectrum indicates that $|E|$ is nearly zero, and one can take the line width of the inner pair of triplet resonances as an upper limit for $|E|$ in this case.

Is the triplet signal attributable to **2**? Although it is unlikely, the triplet signal could be due to a dimer such as **23** or an even higher aggregate. If this latter possibility is so, the triplet signal should disappear when the concentration of **16a** is diminished. When the concentration of **16a** was varied more than twentyfold, from 0.15 M to 6.87×10^{-3} M in hexafluorobenzene, there was no change in the appearance of the triplet signal.



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The intensity of the triplet ESR absorption was studied as a function of temperature in order to determine if **2** has a triplet ground state or if **2** has a singlet ground state and possesses a thermally accessible triplet state. For a ground state triplet, the intensity (I) of the triplet absorption should vary inversely with the absolute temperature (T), and, consequently, the product IT should remain constant with changing temperature (Curie law[28]). If, on the other hand, the triplet were not the ground state of the molecule, but instead had energy ΔE above the ground state, then the intensity of the triplet signal will also change as the population of the excited triplet state changes. In this case the product IT will increase with increasing temperature, and the equation $IT = (e^{-\Delta E/RT})/(1 + 3e^{-\Delta E/RT})$ will be obeyed.[41]

The intensity of the triplet resonance lying to the left of the $g = 2$ radical absorption was measured as a function of temperature for various temperatures in the range −140 to −177 °C. The peak-to-peak height of the resonance line was taken as a measure of the intensity at each temperature, because the line width of the resonance line was observed to remain constant over the temperature range studied. Changes in intensity of the triplet resonance with temperature were not completely reversible due to the detectable decay of **2** in this temperature range. To correct for changes in the intensity due to the decay of **2**, the sample was immediately cooled to −177 °C, where the irreversible decay was very slow, after each intensity measurement at a given temperature. After allowing for temperature equilibration, the intensity of the resonance line was measured at −177 °C. In this way the intensity of the resonance at a given temperature could be compared with the intensity of the line at −177 °C within a very short time, thus making negligible any differences in intensities due to decay of **2**. It should also be noted that the intensity of the triplet signal was perfectly reversible if the temperature changes occurred over a short period of time.

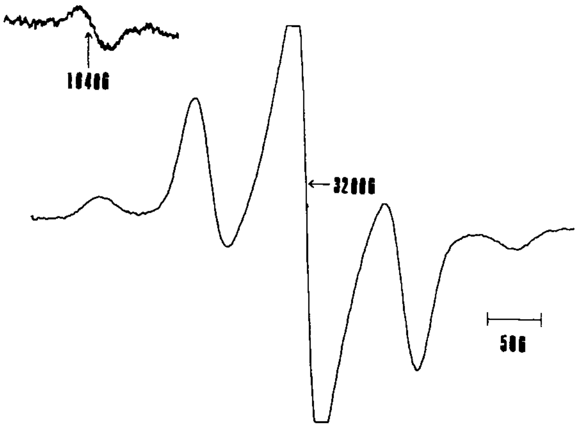


Figure 1. ESR of triplet **2**.

Table II. Determination of Temperature Dependence

Temp (K)	$(IT)_T/(IT)_{94\text{ K}}$ calcd for ΔE (cal/mol)				
	Exptl[a]	100	200	300	400
94	1.00	1.00	1.00	1.00	1.00
101	1.01	1.01	1.04	1.07	1.12
112	1.07	1.03	1.08	1.17	1.28
121	1.10	1.04	1.12	1.24	1.40
131	1.17	1.05	1.15	1.30	1.52

[a] Corrected for irreversible decay of **2**.

In the above study, the product IT of the triplet resonance was found to increase by 14.8% in going from −177 to −140 °C; in contrast, the product IT for the absorption of the radical, where the paramagnetic state is the ground state, remained constant within experimental error (maximum variation 2.7%). These results demonstrate that the triplet state of **2** being detected is not its ground state but rather a low lying thermally accessible triplet state.

The energy difference (ΔE) between the singlet ground state and the triplet excited state could be estimated in the following manner. One could calculate the ratio $(IT)_T/(IT)_{94\,°\text{C}}$ at various temperatures (T) from the experimental data and compare them with the same ratios calculated from eq 1 using various values of ΔE. As can be seen in Table II, the closest fit of the experimental and theoretical ratios occurs when $\Delta E = 200$ cal/mol. Therefore, the triplet state of **2** lies approximately 200 cal/mol above the singlet ground state.

$$\frac{(IT)_T}{(IT)_{94\text{ K}}} = \left(\frac{e^{-\Delta E/RT}}{1 + 3e^{-\Delta E/RT}}\right)_T \Big/ \left(\frac{e^{-\Delta E/RT}}{1 + 3e^{-\Delta E/RT}}\right)_{94\text{ K}} \quad (1)$$

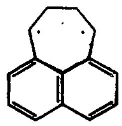
Triplet **2** was observed to decay at −130 °C with an initial half-life of 18 min, but the decay did not follow first-order kinetics. In particular, the decay rate was relatively rapid initially but tapered off at later times (second half-life required approximately 47 min). This result may reflect multiple pathways for the decay of **2**. The initial relatively rapid decay of **2** probably occurs by a process involving species **2** abstracting an atom, perhaps an H atom, from trace hydrocarbon impurities in the solvent to form a radical species. That this process is occurring is evidenced by a significant increase in the intensity of the $g = 2$ radical resonance at the same time that the triplet intensity is decreasing. Other molecules of **2** in the rigid matrix may not be located at a suitable distance or with a suitable orientation to abstract an atom from a donor molecule; in this case, the mode of decay may involve a slower unimolecular mechanism in which **2** is converted to **17** and/or **18**.

The result that the zero-field splitting parameter E for species **2** is zero or nearly zero ($|E| < 0.003\ \text{cm}^{-1}$) is of interest because the quantity E is related to the difference between the squares of the x and y components of the average distance between the two unpaired electrons, according to the equation[29]

$$E = \tfrac{3}{4}g^2\beta^2\langle(y^2 - x^2)/r^5\rangle \qquad (2)$$

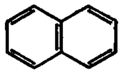
where g = g factor of electron, β = Bohr magneton, $\langle(y^2 - x^2)/r^5\rangle$ = average over the electron function. In the case of a triplet species having a three-fold or higher axis of symmetry, the x and y directions are equivalent and $E = 0$ for these cases. Triplet **2**, however, lacks axial symmetry and one would not a priori expect a zero E in this case.

Apparently the average x and y components of the distance between the two unpaired electrons are nevertheless approximately the same, even though higher symmetry is lacking in this species. This result can be qualitatively understood by comparison of triplet **2** with the naphthalene triplet (**24**). In naphthalene triplet, the x component of the average distance between the two unpaired electrons is expected to exceed the value for the y component, and consequently $E < 0$ for this species.[30] Introduction of the two methylene groups at positions 1 and 8 to form species **2** can be expected to increase considerably the average y component of this distance between unpaired electrons, without affecting to as great an extent the average x component. If the resulting increase in the average y component makes it essentially the same as the average x component, then E will be zero or nearly zero. This is not a new phenomenon in this case, for triplets lacking a threefold axis of symmetry and possessing an E of zero are known.[31]



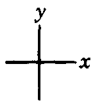
2

$|D| = 0.018\ \text{cm}^{-1}$
$|E| < 0.003\ \text{cm}^{-1}$



24

$D = 0.1003\ \text{cm}^{-1}$
$E = -0.0137\ \text{cm}^{-1}$



Another point of interest concerns the weak intensity of the low-field ($\Delta M = \pm2$) transition of **2**. This transition typically has a greatly reduced transition probability in comparison with the upfield transitions ($\Delta M = \pm1$). For a triplet randomly oriented in a matrix, however, the intensity of the former transition is often comparable with or greater than those of the $\Delta M = \pm1$ transitions, because the anisotropy associated with the former resonance is usually much less than that of the latter. In the case of **2**, the weak intensity of the low-field transition may result from an abnormally low transition probability. Other reports of triplets having weak low-field resonances have appeared in the recent literature.[5b,32]

When **16a** was irradiated in an ethanol glass, the same triplet was observed in the ESR spectrum as was observed in hexafluorobenzene. The only noticeable difference between the two spectra was the greatly diminished amount of the radical near $g = 2$ seen in ethanol. The fact that the triplet is observed in the ethanol glass is particularly exciting because, as already noted, both **17** and **18** are formed under these conditions when **16a** is photolyzed. Thus, at least part of the overall reaction does proceed through a triplet electronic state of **2**.[33] Because one cannot correlate the intensity of the ESR signal with the amount of quinodimethane present, however, the amount of reaction proceeding through this triplet is not known.

There is at least one other method which might yield this observable electronic state of **2**. Meinwald has shown[8c] that irradiation of 1,8-divinylnaphthalene (**18**) affords two products, one of which is naphthocyclobutane (**17**). Furthermore, this photoisomerization may well proceed via the triplet excited state of **18**.[34] Because of this, irradiation of **18** in ethanol glass might afford triplet **2**. Unfortunately, when the ESR experiment was run, no signals of any kind were observed. Attempted preparative irradiation of **18** in ethanol glass at liquid nitrogen temperature was also fruitless; no products were observed. It is likely that the molecule exists in a conformation in the rigid medium from which the terminal carbons cannot reach and form **2**.

Discussion

How is it possible to tie all the pieces of information together and form a coherent and believable mechanism for the conversion of **16** into **17** and **18**? Just consider, for example, that the intermediate in this reaction, **2**, can exist in at least three conformations, any one of which can have a singlet and triplet electronic state. Furthermore, any of these singlet and triplet conformers can interconvert with each other and isomerize to either of the observed products. A priori, then, there are a huge number of ways that **16** can be converted into **17** and **18** and still accommodate the experimental data. With the judicious use of MO calculations, the principle of least motion, and overlap considerations, one can arrive at a believable scheme which explains all our results.

Although one could make a case for concerted expulsion of nitrogen from **16** in the thermal reaction (negative $\Delta S^{\ddagger}$), the mode of nitrogen loss from **16**, either thermally or photochemically, does not seem to be a critical factor in explaining the dynamic behavior of **2**. Consider that the concerted loss of nitrogen from **16** would form the bent conformer **22**. This species alone cannot be responsible for the formation of **17** and **18**, for it would afford the incorrect distribution of deuterium in these hydrocarbons (**17b** and **18b** would be formed). Even if this conformer were formed initially, it would have to interconvert to other conformers of **2** more rapidly than it isomerizes to **17** and **18** in order to explain the observed deuterium distribution. It probably does not matter very much on which part of the energy surface of **2** is reached initially, because the same products and distribution of deuterium will always result if the equilibration of the conformers is rapid.

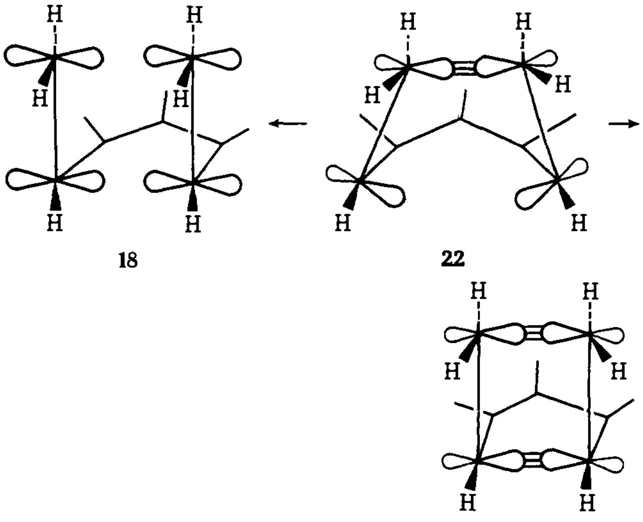
Molecular models suggest that there are likely two candidates for the conformers of **2** observed in these reactions. These are the twist and bent conformers, **21** and **22**, respectively. The planar conformer (**20**) seems a much less likely candidate because of anticipated angle strain in the seven-membered ring. To verify our judgment on this matter, CNDO/2 and INDO calculations were performed[35] on the singlet and triplet electronic states of these conformers. Our model of each species used the known bond lengths and angles of naphthalene as well as "normal" bond lengths and angles for the remaining atoms. Although our model is crude and the use of the CNDO/2 and INDO calculations may be suspect in molecules so large, as seen in Table III, the planar conformer is consistently much higher in energy for a particular electronic state and method of calculation than **21** and **22**. We thus reject **20** as the intermediate in the decomposition of **16** and turn our attention to **21** and **22**, where a choice based on the calculations is not reasonable.

If one looks at a model of **22**, it is clear that the nonbond-

Table III. Calculated Binding Energies (Atomic Units)

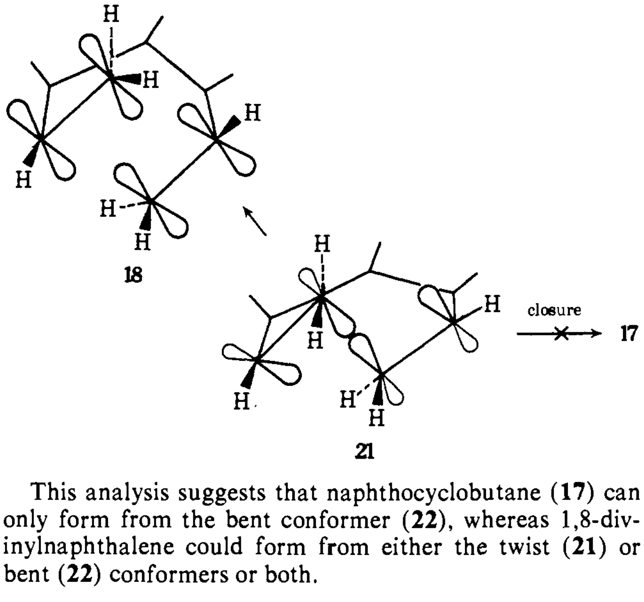
Method of calculation	Electronic state	Conformer 20	21	22
CNDO/2	Singlet	−14.415	−14.671	−14.511
CNDO/2	Triplet	−14.582	−14.676	−14.658
INDO	Singlet	−14.146	−14.379	−14.247
INDO	Triplet	−14.246	−14.314	−14.323

ed orbitals on the methylenes attached to C-1 and C-8 of the naphthalene ring face toward each other. With minimal effort, these orbitals can move toward each other, bond, and form **17**. A slightly different perspective of **22** also shows that the nonbonded orbitals are aligned with the σ bond joining the two bridging methylene groups. Stretching and breaking this σ bond would afford **18**, again with a minimal displacement of nuclei.



18 **22** **17**

A similar analysis of the twist conformer (**21**) reveals that the nonbonded orbitals also overlap with the σ bond joining the bridging CH_2's, although not as well as in conformer **22**. Rupture of this σ bond would then afford **18**. Unlike **22**, **21** cannot afford the naphthocyclobutane (**17**) directly. It would have to contort essentially back to **22** before **17** could be formed.



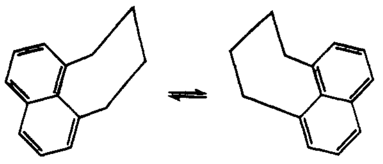
18 **21**

This analysis suggests that naphthocyclobutane (**17**) can only form from the bent conformer (**22**), whereas 1,8-divinylnaphthalene could form from either the twist (**21**) or bent (**22**) conformers or both.

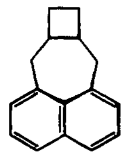
Let us now tie these facts together and see what happens when the deuterated azo compound **16b** extrudes nitrogen (see Scheme III). For the moment, assume that the process is concerted and **22a** is formed. Although this moiety can afford both products, it is clear from previous consideration that it alone cannot afford them because the wrong distribution of deuterium would result. Only if **22a** is converted rapidly to **22b** can the correct deuterium distribution be obtained. With the aid of a molecular model, the conformational interconversion of **22a** and **22b** can be seen to be facile, so long as the interconversion proceeds through **21a**. On the other hand, if **21a** had formed first, it could only afford 1,8-divinylnaphthalene (**18d**). Only if **21a** rearranged to **22a** and **22b** can any naphthocyclobutane be formed.

Three points merit mention about this mechanism. First, the correct distribution of deuterium in **17** and **18** can only result if **21a, 22a**, and **22b** equilibrate much more rapidly than they are converted to **17** and **18**. Second, if the equilibration is rapid, it will not matter where a reactant reaches the energy surface of **2**; **2** will always yield essentially the same ratio of products d deuterium in these products. Third, in theory one has a method for determining the extent to which **21** and **22** open to form 1,8-divinylnaphthalene, because a 50:50 mixture of **22a** and **22b** would form a 50:50 mixture of **18b** and **18c**, while **21a** would form **18d**, exclusively. Unfortunately, there is no obvious way of distinguishing a 50:50 mixture of **18b** and **18c** from **18d**. Only with the use of label other than deuterium, where the isomers can be separated, can this point be clarified.

A mobile equilibrium similar to that proposed for **2** has precedent in the work of Nelsen and Gillespie.[36] By analysis of the temperature-dependent NMR of **25** and the ESR spectra of the radical anions of **25** and **26**, these workers concluded that **25** exists primarily in a bent conformation and undergoes a rapid interconversion to an equivalent bent form, presumably via a twist conformer.



25 **25**

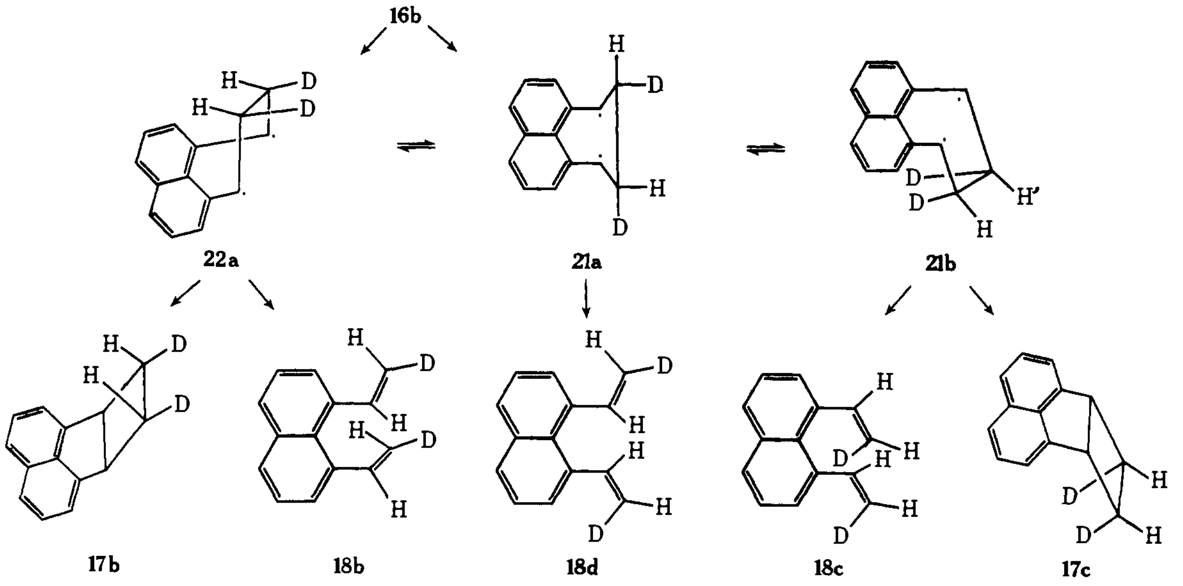


26

The photodecomposition of **16a** and **16b** in ethanol glass can also be accommodated by the scheme which we used to explain the fluid solution behavior. The random distribution of deuterium observed in the products formed in this medium is nicely explained by the scheme. Because the scheme is fairly complex, however, it is difficult to explain why the product distribution is so different in this case. Perhaps because the rates of conformer interconversion and reaction are slow at this low temperature, product formation may depend on the rate of thawing the ethanol glass.

Why does **2** have a singlet ground state rather than the predicted triplet one? In a molecule this complex, it is difficult to say with certainty, although one or more of the following reasons may apply. The first of these is the Jahn–Teller effect,[37] where a vibration (distortion) of the correct symmetry will cause the degenerate MO's at $E = 0$ to split. Second, molecules which have two electrons distributed over two degenerate molecular orbitals do not necessarily have a triplet ground state even in the absence of distortion. Whether a singlet or triplet is the ground state will depend upon the sign of the molecular exchange integral for the two degenerate molecular orbitals. If this integral is positive, a singlet ground state will result, e.g., coronene dianion.[38] And third, allowance for a weak interaction (overlap) between the nonbonded orbitals on the radical centers

Scheme III



will cause the degeneracy of the highest occupied molecular orbitals to split, and a singlet ground state will be predicted in this case. This last notion has been verified by Hückel calculations on **2** and is a very plausible explanation for the singlet ground state because there must be some overlap between the close radical centers on **2**. As far as known, this third criterion is unique to the 1,8-naphthoquinodimethane and merits further exploration.

In conclusion, we have generated a 1,8-naphthoquinodimethane which has a triplet state only slightly above the singlet ground state in remarkable agreement with the Hückel prediction. Furthermore, this species is conformationally mobile, rapidly interconverting between a bent and a twist conformation. The relative energy of the bent and twist conformation and which of these gives rise to the observed triplet cannot be unambiguously answered from the present study.[42]

Experimental Section

General Procedures. Melting points are uncorrected. NMR spectra were recorded on Varian A-60 and HA-100 spectrometers. Infrared spectra were recorded on a Perkin-Elmer IR 5A instrument. Mass spectra were recorded on a Perkin-Elmer RMU-6E spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn.

Reaction of Phenalenone (4) with Dimethyloxosulfonium Methylide (5). A solution of 22.9 mmol of dimethyloxosulfonium methylide[13] in 25 ml of Me_2SO was added with stirring to a solution of 44.8 mmol of phenalenone[12] in 30 ml of Me_2SO under nitrogen over a 45-min period. The resulting dark solution was heated at 55 °C for 30 min and cooled.

Standard work-up gave an orange oil which was chromatographed very carefully on a 5 × 75 cm alumina column. Elution with 20% ether-ligroine afforded three compounds. The first one eluted contained a trace of a yellow solid which was not characterized. The second compound, a bright orange solid weighing 2.0 g, was identified as 9-methylphenalenone (**8**) (vide infra). Further elution afforded 3.0 g of unreacted phenalenone.

Sublimation and recrystallization (twice) from cyclohexane-ether of the chromatographed 9-methylphenalenone afforded 1.0 g (23% yield) of analytically pure ketone, mp 94-95 °C (lit.[39] 91-93 °C).

The bright-yellow compound showed: ir (CCl_4) 1639 cm^{-1}; NMR (CCl_4) δ 7.22-7.95 (m, 6 H, arom), 6.3 and 6.46 (half of an AB q, 1 H, H-2, $J = 10$ Hz), and 2.87 (s, 3 H, methyl).

Anal. Calcd for $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found: C, 86.74; H, 5.19.

Reaction of 9-Methylphenalenone (8) with Dimethyloxosulfonium Methylide (5). A solution of 1.73 mmol of dimethyloxosulfonium methylide in 7 ml of Me_2SO was added with stirring to a solution of 319 mg (1.64 mmol) of 9-methylphenalenone in 5 ml of Me_2SO under nitrogen over a 20-min period. The resulting green solution was heated at 50 °C for 1 h.

The usual work-up afforded a dark oil which was charomatographed on a 3 × 75 cm Florisil column. Elution with 15% ether-ligroine afforded 108 mg of a yellow oil identified as 9-methyl-2,3-homophenalenone (**9**). Further elution gave 114 mg of recovered 9-methylphenalenone.

The yellow oil above was molecularly distilled (100 °C, 0.1 mm). The resulting very pale-yellow oil gave: ir (CCl_4) 1666 cm^{-1} (C=O); NMR (CCl_4) δ 7.13-7.73 (m, 5 H, arom), 2.27-2.98 (m, 5 H, H-3, H-2, and methyl), 1.17-1.70 (m, 1 H, H-10 exo), and 0.70-1.03 (m, 1 H, H-10 endo).

Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81; Found: C, 86.46; H, 5.86.

Reaction of Phenalenyl Anion (11) with Methylene Chloride/*n*-Butyllithium. To a solution of 12.20 g (0.0734 mol) of phenalene[14] in 1500 ml of ether was added under nitrogen 60.0 ml of 1.5 N (0.090 mol) of *n*-butyllithium over 2 h. After the addition was complete, the bright-red solution was stirred at room temperature for 1 h and then cooled to −70 °C. With rapid stirring was added 20 ml of methylene chloride over 1 h. This was followed by the addition of 80.0 ml of 1.5 N (1.20 mol) *n*-butyllithium over 3 h. During the addition of the methylene chloride and *n*-butyllithium, the temperature of the red solution was maintained between −65 and −70 °C. After warming to room temperature, 400 ml of H_2O and 200 ml of $CHCl_3$ were added to the reaction mixture. The organic phase was separated, dried, and removed in vacuo, leaving 16.06 g of a dark-red oil. Chromatography on a 3 × 30 cm alumina column (eluting with ligroine) afforded 8.95 g of a crystalline solid shown by NMR to contain 84% of 1,8-naphthotricyclo[4.1.0.0^{2,7}]heptene (**12**) and 16% of pleiadiene (**3**).

To separate **12** cleanly and easily from **3**, 5.90 g of the above mixture was refluxed for 36 h in a solution containing 6.00 g (0.0345 mol) of diethyl azodicarboxylate in 20 ml of CCl_4. After removing the solvent in vacuo, the viscous oil was chromatographed on a 2 × 25 cm alumina column. Eluting with 2.0 l. of ligroine afforded 4.95 g of **12** whose characterization is described below. Elution with 2.0 l. of 50% ether in ligroine afforded 1.50 g of an oil shown to be the Diels-Alder adduct of pleiadiene and diethyl azodicarboxylate (vide infra).

The 4.95 g of **12** was recrystallized from ligroine to afford analytically pure material: mp 76.5-77.0 °C; NMR (CCl_4) δ 6.83-7.50 (m, 6 H, arom), 2.20 (t, 2 H, central methine, $J = 2.5$ Hz), and 2.93 (t, 2 H benzyllic methine, $J = 2.5$ Hz).

Anal. Calcd for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.56; H, 5.48.

In an alternate procedure, the mixture of **12** and **3** was recrystallized repeatedly from ligroine until the NMR indicated the presence of only **12**.

Preparation of [1′,8′]Naphthobicyclo[3.2.0]hepta-2,6-diene. A sealed (in vacuo) NMR tube containing 41.0 mg of **12** in 0.4 ml of cyclohexane was immersed in an oil bath at 128 °C for 30 min. NMR showed change. On heating at 150 °C, a reaction was seen to occur by periodic inspection of the NMR. After 18 h, the tube was opened and the solvent removed in vacuo. Chromatography of the residue on alumina afforded 30.0 mg of [1′,8′]naphthobicyclo-[3.2.0]hepta-2,6-diene (**14**). After recrystallization from ligroine and sublimation, the white crystals had mp 117–118 °C identical with authentic material[11] (lit.[11] mp 118–119 °C).

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

Preparation of Pure Pleiadiene (3). A solution of 4.01 g of an admixture containing 67% of **12** and 33% of pleiadene (**3**) in 125 ml of ligroine was pyrolyzed at 500 °C in flow tube packed with glass beads. The effluent was collected in a series of three traps cooled in dry ice–acetone. Collecting the solutions and removal of the solvent left a red residue which was chromatographed on a 3 × 30 cm alumina column, eluting with ligroine; the fraction size was 500 ml. Fractions 3–8 contained 3.32 g (83% yield) of pleiadiene. Recrystallization from hexane gave analytically pure pleiadiene, mp 88–90 °C (lit.[10] 87–90 °C).

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

Photolysis of 12. A solution of 37.0 mg of **12** in 100 ml of cyclohexane under N_2 was irradiated at 2537 Å for 5 h. Work-up showed that **12** had been converted completely to pleiadiene. Comparable photolysis of **12** in benzene at 2537 Å also afforded pleiadiene.

Isomerization of 12 to Pleiadiene Using Iodine. In an NMR tube containing 33.0 mg of **12** in 0.3 ml of CCl_4 was added 5.0 mg of I_2. There was an instantaneous color change. The NMR showed only the presence of pleiadiene. Work-up and chromatography of the residue on alumina afforded 22.0 mg of pleiadiene.

Stability of 12 to Diethyl Azodicarboxylate. In an NMR tube was placed a solution containing 0.24 mmol of **12**, 0.35 mmol of diethyl azodicarboxylate, and 0.35 mmol of anisole (internal standard) in 0.4 ml of CCl_4. The tube was capped and heated at 70 °C. Periodically, the tube was cooled and checked for anisole and bicyclobutane (**12**). The following relative amounts of anisole and **12** were found: $t = 0$, 59%, 41%; 19.5 h, 63%, 36%; 47.3 h, 64%, 36%; 69.1 h, 63%, 37%.

Stability of 12 to *N*-Phenyltriazolinedione. A solution of 49.0 mg (0.275 mmol) of **12** and 50.0 mg (0.283 mmol) of *N*-phenyltriazolinedione in 5 ml of CH_3CN was allowed to stand at room temperature for 19 h. After removing the CH_3CN, the residue was redissolved in CH_2Cl_2. Analysis of the NMR revealed that **12** had not reacted. No peaks attributable to other compounds were observed.

Naphtho[1′,8′]bicyclo[3.2.0]hept-2-ene (17a). A solution of 1.70 g (9.54 mmol) of **14** and 0.050 g of Adam's catalyst in 15 ml of 95% ethanol was subjected to atmospheric hydrogenation for 24 h. The solution was filtered through Celite and the solvent removed in vacuo. The product was chromatographed on a silica gel column (2 × 15 cm) and eluted with ligroine. Fractions of 100 ml were collected and fractions 1–4 contained 1.34 g (77.9%) of product. Recrystallization from ethanol and sublimation gave pure **17a**: mp 74.5–75.5 °C (lit.[8c] 74.0–75.5 °C); NMR (CCl_4) δ 7.45 (m, 6 H, arom), 4.20 (m, 2 H, benzyllic) 2.70 (m, 2 H, exo CH_2), and 1.85 (m, 2 H, endo CH_2); mass spectrum (10 eV) *m/e* (rel intensity) 180 (77), 152 (100).

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

Naphtho[1′,8′]bicyclo[3.2.0]hept-2-ene-d_2 (17b). A 0.500-g (2.81 mmol) sample of **14** was dissolved in 5.00 ml of CH_3OD in a dry nitrogen atmosphere. To this stirred solution was added 1.086 g (5.59 mmol) of potassium azodicarboxylate[40] and 0.40 ml (6.9 mmol) of DOAc, followed by two 2.00-ml portions of CH_3OD. The mixture was stirred for 30 min and then recharged six times at 30-min intervals with 0.25 ml (4.3 mmol) of DOAc and 0.25 g (5.1 mmol) of potassium azodicarboxylate. The reaction mixture was stirred for 12 h and the solvent removed in vacuo. The product was chromatographed on an alumina column (2 × 20 cm) which was eluted with ligroine (100-ml fractions). Fractions 1–2 contained no product. NMR analysis of fraction 3 showed it to contain 0.290 g of a mixture consisting of 95% of product and 5% unreacted starting material. Fraction 4 contained 0.150 g of material contained 84% product and 16% starting material. Subsequent fractions contained only a small amount of hydrocarbon (0.020 g) consisting of 70% of **17b** and 30% of **14**. Fractions 3–4 were rechromatographed on alumina (3 × 80 cm) and 100-ml fractions collected. Fractions 1–12 contained no product and fractions 13–16 contained 0.171 g of pure **17b**. Subsequent fractions were contaminated with **14**.

NMR analysis indicated complete deuteration of the double bond: δ 7.45 (m, 6 H, arom), 4.15 (br s, 2 H, benzyllic), 1.85 (d, 2 H, J = 4Hz).

Examination of the NMR of pure **17b** revealed that the signal at δ 2.70 in the deuterated product had completely disappeared. Since the protons anti to the bridgehead protons are in the shielding cone of the aromatic ring, they should be upfield relative to the syn protons, which are relatively unaffected by the ring current. On this basis the deuterium added cis and syn relative to the bridgehead protons.

Synthesis of 13. This compound was obtained in two ways. In the first procedure, **13** is obtained in the purification of **12** (vide supra).

In the second procedure, a mixture of 2.80 g (15.7 mmol) of pleiadiene (**3**) and 3.00 g (17.2 mmol) of diethyl azodicarboxylate was dissolved in 100 ml of benzene and refluxed for 18 h under dry N_2. The reaction mixture was cooled and the solvent removed in vacuo. The resulting orange oil was chromatographed on an alumina column (3 × 30 cm) and 250-ml fractions were collected. The column was eluted with 1 l. of 4% ether in ligroine, 1 l. of 10% ether and 2 l. of 50% ether. Fractions 1–4 contained a small amount of red solid (less than 10 mg), fractions 5–8 contained unreacted diethyl azodicarboxylate, and fractions 9–16 contained 3.80 g (67.7%) of **13**. A small amount of this glassy material was sublimed for analysis: ir (CCl_4) 5.90 μ (C=O); NMR (CCl_4) δ 7.50 (m, 6 H, arom), 6.46 (m, 2 H, vinyl), 5.94 (m, 1 H, bridgehead), 5.59 (m, 1 H, bridgehead), 4.17 (q, 2 H, methylene, J = 7 Hz), 3.80 (q, 2 H, methylene, J = 8 Hz), 1.22 (t, 3 H, methyl, J = 8 Hz), and 0.82 (t, 3 H, methyl, J = 7 Hz).

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

Synthesis of 15a. To a solution of 1.274 g (3.62 mmol) of **13** in 10 ml of 95% ethanol was added 20 mg of Adam's catalyst. The mixture was then subjected to low-pressure hydrogenation for 24 h. The solution was then filtered through Celite and the solvent removed in vacuo. The resulting oil was chromatographed on silica gel (3 × 30 cm) eluting with 1.125 l. of 10% ether in ligroine, followed by 1.125 l. of 50% ether. Fractions 6–10 contained 1.115 g (85.5%) of **15a**, which was a glassy solid. A small sample was taken for analysis and sublimed twice in vacuo: ir (CCl_4) 5.90 μ (C=O); NMR (CCl_4) δ 7.53 (m, 6 H, arom), 5.60 (br s, 1 H, bridgehead), 5.16 (br s, 1 H, bridgehead), 4.23 (q, 2 H, methylene, J = 6 Hz), 3.60 (q, 2 H, methylene, J = 7 Hz), 2.30 (m, 4 H, CH_2CH_2), 1.28 (t, 3 H, methyl, J = 7 Hz), and 0.76 (t, 3 H, methyl, J = 6 Hz).

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

Synthesis of 15b. To a solution of 1.527 g (4.31 mmol) in **13** in 5.0 ml of CH_3OD under dry N_2 was added 2.97 g (11.2 mmol) of potassium azodicarboxylate[40] and 0.70 ml (4.59 mmol) of DOAc, followed by two 2.0-ml portions of CH_3OD. The solution was stirred for 30 min and recharged ten times at 30-min intervals with 0.50 g (2.57 mmol) of potassium azodicarboxylate and 0.25 ml (4.2 mmol) of DOAc. The solution was stirred under N_2 for 12 h and the solvent removed in vacuo. The product was chromatographed on silica gel (2 cm × 20 cm) eluting with 500 ml of ligroine followed by 1 l. of 50% ether in ligroine; fraction size ws 250 ml. Fractions 3–6 contained 1.390 g (90.5%) of **15b**. It was not possible to determine the stereochemistry from the NMR; NMR (CCl_4) identical with **15a** except the multiplet at δ 2.30 now integrated for 2 H.

Synthesis of 16a. A 0.550-g (1.55 mmol) sample of **15a** was dissolved in 25 ml of methanol and 5 ml of water containing 5.0 g (89.3 mmol) of potassium hydroxide. The mixture was refluxed for 3 h under nitrogen and then poured into 100 ml of water and extracted with three 100-ml portions of chloroform. The combined organic layers were dried ($MgSO_4$) and the solvent removed in vacuo. The glassy product was chromatographed on a silica gel column (3 × 20 cm). The column was eluted with 500 ml of ligroine, followed by 500 ml of 50% ether in ligroine; 100 ml fractions were collected. Fractions 7-9 contained 0.180 g (55.9%) of **16a**, which was sublimed giving a glassy solid: uv (cyclohexane) $\lambda_{\max}$ 4110 Å (ϵ 1065); NMR (CCl_4) δ 7.51 (m, 6 H, arom), 6.10 (s, 2 H, bridgehead), and 1.98 (d, 4 H, CH_2CH_2).

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

Preparation of 16b. The procedure was analogous to the preparation of 16a: NMR (CCl_4) δ 7.46 (m, 6 H, arom), 6.15 (s, 2 H, bridgehead), 2.10 (s, 2 H, CHDCHD).

Eu(fod)$_3$-d_{30} Studies on 16a and 16b. An NMR sample of **16a** and Eu(fod)$_3$-d_{30} in $CDCl_3$ was prepared such that the bridgehead H appeared at δ 10.10: NMR δ 10.10 (s, 2 H, bridgehead), 8.60 (d, 2 H, arom), 8.15 (d, 2 H, arom), 7.74 (t, 2 H, arom), 4.90 (m, 2 H, bridge H syn to azo), and 4.14 (m, 2 H, bridge H anti to azo).

An NMR sample of **16b** and Eu(fod)$_3$-d_{30} in $CDCl_3$ was also prepared such that its bridgehead H appeared at approximately δ 10.10. The bridge H now appeared as a very small singlet at 4.78 and a very intense one at 4.10 ($I_{4.10}/I_{4.78} \geq 15$). Because the signal at δ 4.78 is due to H syn to azo, these sites are now predominantly D. Because there is so little H at the syn position, it was neglected in the discussion although its presence was taken into account in subsequent analysis.

Pyrolysis of 15. General Procedure. A 30-60-mg sample of **16** was placed in an NMR tube, and approximately 0.4 ml of the desired solvent was added. If an internal standard was desired, a small amount of Me_4Si was added. In general, the sample was then degassed by repeated "freeze-pump-thaw" cycles and the tube sealed (except samples decomposed in air). The NMR spectrum was recorded, and the sample was then placed in an oil bath maintained at the desired temperature. The sample was removed at 15-30-min intervals, if desired, cooled, and the NMR recorded in order to monitor the appearance of product and the disappearance of the initial azo compound. At the end of the pyrolysis, the tube was cooled and opened, and the contents were chromatographed on silica gel (3 × 30 cm). A summary of the results can be found in Table I.

Control Studies in the Pyrolysis of 16. A sample of **17b** in tetrachloroethylene was prepared as described above and placed in an oil bath (134 °C). The sample was removed after 15 min, 30 min, 1 h, and 2 h, cooled, and the NMR recorded. No change in the NMR could be discerned. **17b** had not undergone stereorandomization or produced any detectable amount of 1,8-divinylnaphthalene-d_2.

A mixture of 53% **17a** and 47% **18a** in tetrachloroethylene was prepared as described above and placed in an oil bath (134 °C). The sample was removed after 15 min, 30 min, 1 h, and 2 h of pyrolysis, and cooled, and the nmr was recorded. The ratio **17a**/**18a** was found to be invariant with time.

Samples of **16a** in hexafluorobenzene and tetrachloroethylene were prepared and Me_4Si was added. The samples were degassed, sealed, and immersed in an oil bath at 134.0 °C. The total amount of reactant and product was monitored as a function of time and was found to be constant within the limits of integration. Further, the ratio of **17a** to **18a** was constant within the limits of integration.

Photolysis of 16. General Procedure. The samples were prepared as previously described. Photolyses were run in a Rayonet Preparative Photochemical Reactor using 3500-Å lamps with no filters. After taking an NMR, the photolysis was started and the sample removed at 15-30-min intervals to monitor the reaction by NMR. Upon completion of the photolysis, the tube was opened, and the products were chromatographed on silica gel. Results are summarized in Table I.

Low-Temperature Photolysis of 16. The sample to be photolyzed was dissolved in approximately 50 ml of the desired solvent, and the solution was placed in the cooling jacket of a Hanovia photochemical reactor. The lamp well was cooled with dry ice-acetone or liquid nitrogen as necessary. The reactor well was evacuated, and the entire assembly was placed in the well of a Rayonet Photochemical Reactor and irradiated at 3500 Å using no filters. Upon completion of irradiation, the system was allowed to warm to room temperature and worked-up in the usual manner.

Control Studies in the Photolysis of 16. A sample of **17b** in tetrachloroethylene was prepared and irradiated with 3500-Å light for 2 h. The sample was removed from the reactor after 15 min, 30 min, 1 h, and 2 h irradiation and the NMR recorded. No change could be discerned in the sample.

A mixture of 52% **17a** and 48% **18a** in degassed tetrachloroethylene with Me_4Si was prepared and irradiated with 3500 Å light for a period of 2 h. The sample was removed after 15 min, 30 min, 1 h, and 2 h irradiation and the NMR recorded. The ratio of **17a** to **18a** was found to be invariant with time as was the total amount of material within the limits of integration.

Trapping Experiments. The thermal reactions were run on 60-80-mg samples of **16a** dissolved in 50-75 ml of CCl_4 with a 10 to 15-fold excess of diylophile added. Pyrolysis samples were prepared by the freeze-pump-thaw procedure and decomposed at 135 °C. Photolyses at 3500 Å were run in NMR tubes as previously described; a 10- to 15-fold excess of diylophile was used. Product analyses were accomplished by a combination of NMR and chromatography on silica gel.

Accurate product ratios were not possible because of NMR overlap and slow decomposition of **18** on workup. The ratios are approximately the same as those previously described, however.

Kinetics of Pyrolysis of 16a. A 16-20-mg sample of **16a** was placed in a 100-ml volumetric flask, and tetrachloroethylene was added to the mark. The solution (3.00 ml) was then pipeted into vials which were degassed by repeated "freeze-pump-thaw" cycles and sealed. The sealed vials were placed in a thermostated bath at the desired temperature. The vials were removed at the required intervals and quenched by plunging into cold water. The vials were then opened, and the rate of disappearance of **16a** was monitored by disappearance of the n,π* transition of **16a** at 4110 Å (ϵ 1065). Both products had extinction coefficients of less than 10 at this wavelength. Rate constants of 1.88×10^{-4} s^{-1} (128.8 °C), 2.96×10^{-4} (134.0 °C), and 7.41×10^{-4} (145.0 °C) were obtained.

Product Identification. The hydrocarbon products, **17a** and **18a**, from several photochemical and pyrolytic decompositions of **16a** were combined giving 190 mg of material which was placed on a 5% silver nitrate-silica gel column (2 × 30 cm). The column was eluted with 1 l. of ligroine and 1 l. of 10% ether in ligroine, and 100-ml fractions were collected. Fractions 1-5 contained 150 mg of **17a**, which was crystallized from methanol and compared with authentic material. NMR spectra, melting point, and undepressed mixed melting point showed the isolated material to be **17a**. Fractions 13-17 contained 30 mg of **18a**, which was compared with authentic material. NMR, melting point, and undepressed mixed melting point showed the isolated material to be **18a**.

NMR Analysis of Deuterated Products. Analysis of 17. The area of interest consisted of δ 4.20 (br s, bridgehead), 2.70 (d, endo bridge H, J = 10 Hz), and 1.85 (d, exo bridge H, J = 4 Hz) in a ratio approximately 2:1:1. This is consistent with a mixture of 50% **17b** and 50% **17c**.

Analysis of 18. To aid in interpreting the NMR of deuterated **18**, the NMR of **18a** will be presented: NMR (CCl_4) δ 7.60 (m, 8 H, arom + 2 vinyl), 5.52 (d of d, 2 H, trans vinyl, J = 17, 3 Hz), and 5.27 (d of d, 2 H, cis vinyl, J = 10, 3 Hz).

The area of interest in the deuterated **18** consisted of δ 5.50 (d, J = 17 Hz) and 5.23 (d, J = 10 Hz) in a ratio close to 1:1. This is consistent with a 50:50 mixture of **18b** and **18c**.

Pyrolysis of 16a in the Probe of NMR. Samples were prepared by dissolving **16a** in 1-chloronaphthalene. Pyrolyses were carried out at both 140 and 200 °C inside the probe of a Varian HA-100 spectrometer. No CIDNP was detected in these runs.

Preparation of ESR Samples. An accurately weighed quantity of **16a** was added to a 4-mm quartz ESR tube, and the sample was dried for 10 min in vacuo. A measured volume of solvent was introduced into the ESR tube with a syringe, and the sample was then degassed by carrying out at least four freeze-thaw cycles on a high-vacuum line. The ESR tube was then sealed off in vacuo at a pressure <1 μm. Reagent grade absolute ethanol and hexafluorobenzene were used without further purification in preparing these samples.

Generation of the 1,8-Naphthoquinodimethane for ESR Study. ESR studies were carried out using a Varian V-4500 ESR spectrometer equipped with an optical transmission cavity and either a Varian V-4257 variable-temperature accessory or a quartz sample dewar filled with liquid nitrogen. In a typical experiment, a solution of **16a** was rapidly frozen in liquid nitrogen and then quickly transferred to the cooled cavity dewar. The sample was irradiated without any filters at −160 °C with an Oriel 200-W "super-pressure" mercury lamp, which was positioned such that the front lens of the Oriel irradiation unit was approximately 7 in. in back of the entrance port of the optical transmission cavity. A detectable triplet ESR signal from **2** was typically observed within minutes after the irradiation was initiated.

Intensity Study of Triplet Signal. A sample consisting of 0.15 M solution of **16a** in hexafluorobenzene was used in this study. The intensity of the triplet resonance line lying to the left of the $g = 2$ radical absorption in the observed ESR spectrum was measured as a function of temperature for various temperatures in the range −140 to −177 °C. The temperature settings of the variable-temperature controller were calibrated beforehand using a copper-constantan thermocouple and a Biddle potentiometer. Since the line width of the triplet resonance was observed to remain constant over the above temperature range, the peak-to-peak height of the triplet resonance was taken as a measure of the relative intensity of the triplet signal at a given temperature.

At −177 °C, the triplet signal of the quinodimethane did not decay noticeably over a period of 1 h. Changes in intensity of the triplet resonance with temperature were not, however, completely reversible due to measurable decay of the quinodimethane at somewhat higher temperatures in the above temperature range. To correct for changes in the intensity due to decay, the sample was immediately cooled to −177 °C after each intensity measurement at a given temperature. After allowing at least 5 min for temperature equilibration, the intensity of the triplet resonance line was measured at −177 °C (which served as a reference temperature). This made negligible any differences in the intensities resulting from decay of the quinodimethane. The corrected intensity at a given temperature T was then calculated as follows:

$$(I_{\mathrm{cor}})_T = (I_{\mathrm{meas}})_T \frac{(I_1)_{-177\,^\circ}}{(I_{\mathrm{F}})_{-177\,^\circ}}$$

where $(I_{\mathrm{cor}})_T$ is the corrected intensity at temperature T, $(I_{\mathrm{meas}})_T$ is the measured intensity at temperature T at the beginning of the run, and $(I_1)_{-177\,^\circ\mathrm{C}}$ and $(I_{\mathrm{F}})_{-177\,^\circ\mathrm{C}}$ are the initial reacting (I) and the final reading (F) at −177°C, respectively.

In runs where the intensity was measured at only one higher temperature in the above range, such as at −150 °C, the cycle of measuring intensities at −177, −150, and then at −177 °C again could be completed fast enough such that loss of triplet intensity due to decay of the triplet was negligible, and in this case the changes in intensity with temperature were reversible.

Attempted Generation of Naphthoquinodimethane 2 by Photolysis of 1,8-Divinylnaphthalene in a Glass. A 0.16 M solution of **18a** in hexafluorobenzene was degassed in vacuo (<1 μm) and sealed in a 4-mm quartz ESR tube. The sample was quickly frozen in liquid nitrogen and then placed inside a quartz ESR dewar filled with liquid nitrogen, which in turn was placed inside the optical transmission ESR cavity. The sample at −196 °C was irradiated for 1 h with an Oriel 200-W "super-pressure" mercury lamp. The ESR spectrum of the sample was monitored during this period; no detectable triplet signal from the quinodimethane was observed at any time during this period. A similar result was obtained starting with a 0.08 M solution of **18a** in absolute ethanol.

As a variation of this experiment, a 0.08 M solution of **18a** in absolute ethanol was irradiated for 1 h at −196 °C (sample in quartz dewar filled with liquid nitrogen) in a Rayonet photochemical reactor fitted with 3000-Å lamps. The sample did not exhibit any triplet ESR absorption at −160 °C after this irradiation. Preparative photolyses of **18a** in ethanol at −196 °C were also fruitless.

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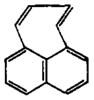

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$$\begin{tikzcd} \mathbf{16} \arrow[r] & \text{singlet } \mathbf{2} \arrow[r, shift left] \arrow[dr] & \text{triplet } \mathbf{2} \arrow[l, shift left] \\ & & \mathbf{17} \text{ and } \mathbf{18} \end{tikzcd}$$

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Protonation Kinetics and Mechanism for 1,8-Dihydroxyanthraquinone and Anthraquinone Anion Radicals in Dimethylformamide Solvent

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Abstract: Protonation of the radical anion of 1,8-dihydroxy-9,10-anthraquinone ($DAQ\cdot^-$) by benzoic acid is first order in acid, second in radical anion, and involves formation of an acid-radical heteroconjugate dimer in an unfavorable, labile equilibrium, followed by rate-limiting electron-transfer reduction of dimer by $DAQ\cdot^-$. Anthraquinone anion radical ($AQ\cdot^-$) is protonated by the Paul-Lipkin-Weissman mechanism with rate limitation shifting to the electron-transfer step at longer reaction times. Both protonation reactions are reversible with modest equilibrium constants.

Introduction

Two-electron electrochemical reductions for aromatic hydrocarbons and quinones in aprotic solvents in the presence of proton donors are classically thought to proceed by the mechanism[2,3]

$$Q + e \rightarrow Q\cdot^- \tag{1}$$

$$Q\cdot^- + HB \rightarrow QH\cdot + B^- \tag{2}$$

$$QH\cdot + e \rightarrow QH^- \tag{3}$$

$$QH^- + HB \rightarrow QH_2 + B^- \tag{4}$$

This mechanism, known as the ECE reaction sequence, was introduced by Hoijtink[4,5] for aromatic hydrocarbons and was extended to quinones by Peover.[6-8] The essential point of the ECE sequence is that the electron affinity of $QH\cdot$ exceeds that of Q (E°_{QH,QH^-} is more positive than E°_{Q,Q^-}), so that reaction 3 proceeds rapidly at electrode potentials causing reaction 1 to occur.

It is now recognized that other reaction mechanisms exist which might kinetically compete with the ECE sequence to yield the same overall products. For example, rather than proceeding heterogeneously at the electrode in reaction 3, the second electron step may proceed through the radical anion

$$QH\cdot + Q\cdot^- \rightleftarrows QH^- + Q \tag{5}$$

This homogeneous electron-transfer pathway was pointed out by Feldberg,[9,10] and observations on it have been reviewed by Saveant.[11] Implicit in both views is overall rate control by reaction 2, written as irreversible and as first order in both radical anion and acid.

Another mechanistic alternative involves disproportionation of the radical anion prior to protonation.[12-14]

$$2Q\cdot^- \rightleftarrows Q + Q^{2-} \tag{6}$$

$$Q^{2-} + HB \rightarrow QH^- + B^- \tag{7}$$

$$QH^- + HB \rightarrow QH_2 + B^- \tag{8}$$

This reaction sequence is perhaps less generally plausible than reaction 5 owing to the very small equilibrium constant ($K_{\rm disp}$) for reaction 6 under most electrochemical conditions.

A number of direct stop-flow kinetic investigations of protonations of aromatic hydrocarbon radical anions by weak acids in aprotic media have appeared in recent years. These studies, made from the physical organic point of view, were conducted principally in tetrahydrofuran and dimethoxyethane solvents and employed alkali metals to generate the radical anions, so that ion pairing effects were important. Sodium naphthalenide was studied by Bank,[15] who identified reaction sequence 2,5,4 as the protonation pathway. This sequence is known as the Paul-Lipkin-Weissman[16] mechanism. Szwarc[17] studied sodium perylenide protonation by water and alcohols in THF and found second-order decay of radical and the sequence 6,7,8. Anthracenide has been extensively examined by Bank,[18] Szwarc,[19] and Dye.[20] A range of protonation rates and mechanisms, including sequences 2,5,4, 6,7,8, and solvation of ion pairs by HB before electron transfer, was observed depending on solvent, acid donor, and alkali metal. The reactions observed ran to completion and were unaffected by the conjugate base of the protonating acid. While none of these investigations were conducted under conventional electrochemical conditions (more polar solvents, no alkali metal cations present), their results do emphasize the need to consider mechanistic alternatives to the ECE sequence in electrochemistry. They also show that reaction 2 cannot implicitly