

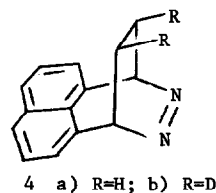
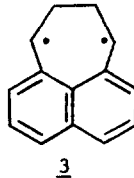
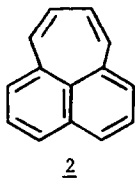
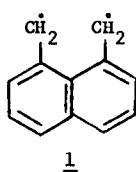
THE BEHAVIOR OF THE SINGLET AND TRIPLET SPIN STATES OF METHYLENE-BRIDGED 1,8-NAPHTHOQUINODIMETHANE WITH O₂

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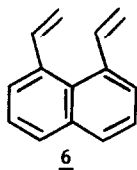
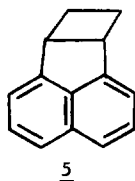
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Abstract—It has been shown that thermolysis of naphthocyclopropane **8** yields the singlet 1,8-naphthoquinodimethane **7** by disrotatory ring opening. In fluid solution the singlet biradical prefers to ring close to regenerate the starting material rather than under a 1,2-hydrogen shift to yield phenalene (**9**). It has been demonstrated that the singlet **7** does not react with O₂ or undergo intersystem crossing to ground state triplet **7**. It has also been shown by an intricate set of experiments that triplet **7** is produced on photolysis of **8** and that it reacts with O₂. Unfortunately, it was not possible to elucidate unequivocally the mechanism by which triplet **7** reacts with O₂.

Some years ago we became interested in the 1,8-naphthoquinodimethane biradical (**1**) (henceforth to be called (O)-1,8-NQM¹) because this species is predicted to have a triplet ground state by simple MO theory.^{2,3} At about this time, we and Murata independently developed an efficient synthesis of pleiadiene (**2**).⁴ As pleiadiene (**2**) has the same carbon skeleton as the ethylene-bridged 1,8-NQM (**3**) ((2)-1,8-NQM) possesses, we set out to convert **2** into the azo compound **4**, the obvious precursor to (2)-1,8-NQM (**3**), and succeeded.⁵ With **4** in hand, we were in a position not only to determine the spin multiplicity of ground state **3** but also to generate and explore the chemistry of the singlet and triplet states of **3**. As summarized below, most of these expectations were realized.



Thermolysis of **4a** at about 140° and photolysis of **4a** at room temperature yielded two isomeric products: the naphthocyclobutane **5** as the major product and 1,8-divinylnaphthalene (**6**).^{5,6} The product ratio, **5**:**6**, was found to be relatively insensitive to solvent and relatively insensitive to mode of decomposition when run in the same solvent.⁵ These results suggest that the product determining step in the thermal and photochemical reactions is the same. When the photochemical decomposition of **4a** was run in MeOH (and CH₂Cl₂) at -77°, the ratio **5**:**6** increased dramatically^{5,7} demonstrating, not surprisingly, that the product determining step has an energy of activation.⁸



Thermolysis and photolysis of deuterated azo compound **4b** in a given solvent yielded **5** and **6** in their normal ratio, with the deuterium "randomized" in each product, i.e. half of **5** had both deuterium atoms *exo* and the other half had both *endo* while half of the D atoms in **6** were *cis* and the other half *trans*. The conclusion from this experiment must be that **3** is an intermediate in both reactions and that it behaves as if it were planar.⁵

When **4a** was irradiated in several glassy matrices at 77K in the probe of an ESR spectrometer, signals characteristic of a triplet ($|D| = 0.018 \text{ cm}^{-1}$, $|E| < 0.003 \text{ cm}^{-1}$) were observed.⁵ That these signals were associated with **3** was borne out by the fact that photolysis of **4a** (and **4b**) under the same conditions, followed by workup, yielded **5** and **6**.⁹ A Curie law study

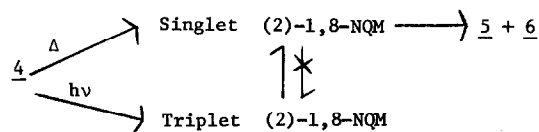
around 77K indicated that the observed triplet was a low lying excited state.⁵ This conclusion was in error.¹⁰ A subsequent Curie law study at liquid He temperatures and a detailed analysis of the UV-VIS spectrum of (2)-1,8-NQM (**3**) and its temperature dependent behavior demonstrated conclusively that the triplet is the ground state.¹¹

Flash photolysis of **4a** in fluid solution¹¹ proved very informative because not only could triplet **3** be detected¹² but also its decay followed as a function of time. Although initially dominated by a second order process, this was followed by a first order decay. Measurement of the first order decay in glycerol at three temperatures yielded: $E_a = 4.5 \pm 0.3 \text{ kcal/mol}$ and $A = 10^{6.9 \pm 0.3} \text{ s}^{-1}$. This enormously low A value indicates that the rate determining step in the decay is the spin forbidden conversion of the triplet ground state into a low lying singlet excited state.

Further flash photolysis work demonstrated that triplet **3** is quenched by O₂ at close to the rate of diffusion.¹¹ Subsequent detailed work of the behavior of **3** with O₂¹⁴

to be reported elsewhere revealed several significant facts: (1) the low lying singlet (2)-1,8-NQM does not react with O_2 , whereas triplet (2)-1,8-NQM, at least in part, reacts to give a peroxide; and (2) singlet (2)-1,8-NQM does not decay to triplet (2)-1,8-NQM.

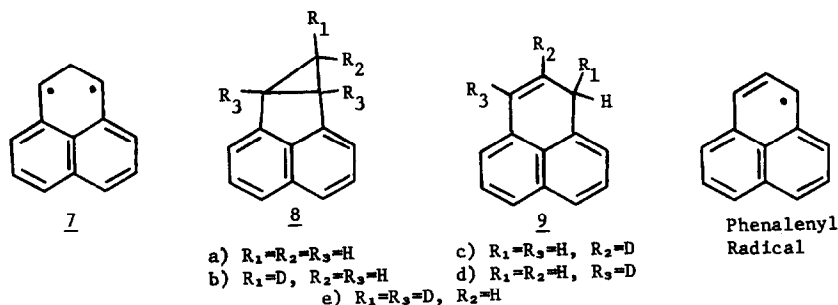
Combining these observations one arrives at the following mechanism.



There are several salient features concerning this mechanism which should be noted at this time. First, the thermolysis of 4 yields singlet (2)-1,8-NQM, while photolysis of 4 yields primarily triplet (2)-1,8-NQM. Second, regardless of the mode of decomposition, the thermal and photochemical reactions have the same product determining step. Third, the conversion of singlet (2)-1,8-NQM into product is much faster than its decay to triplet (2)-1,8-NQM. Fourth, the singlet biradical has not been detected directly. Its existence is proven by all the accumulated data, but most notably by the D distribution in 5 and 6 produced on thermal decomposition of 4b.

Some work has also been reported in the literature on the synthesis and characterization of the methylene-bridged (1)-1,8-NQM (7).^{15,16} Michl and coworkers have shown^{15a} that irradiation of the naphthocyclopropane 8a in a glassy matrix yielded 7, which interestingly has a UV-VIS spectrum very similar to that of 3.¹¹ Just as with 3, 7 yielded an ESR spectrum characteristic of a triplet; Curie law studies of this triplet indicated that it was a low lying excited state. Again, just as with 3, this initial Curie law study was in error; additional work proved that the triplet in fact is the ground state.^{11,17} By observing the decay of the triplet (ESR and UV-VIS) at several temperatures, the activation parameters: $E_a = 4.5 \pm 0.6$ kcal/mol, $A = 10^{4.5 \pm 1}$ s⁻¹ were obtained. The strikingly low A value here also indicates that the rate determining step in the decay is the spin forbidden conversion of the triplet into a singlet, which more than likely is a low lying excited state of 7. Chemical studies in the temperature range 119–133K demonstrated that the decay of 7 yielded the isomeric phenalene (9a), although more complex chemical behavior was observed at higher temperatures and in less viscous media. Here, the phenalenyl radical and possibly 8a were formed in addition to 9a.

In addition to the above work, Roth and Enderer^{15b} have studied the thermally induced epimerization of 8b and these authors speculated that the automerization proceeds through the intermediacy of (1)-1,8-NQM (7), although there was no evidence presented which would exclude a mechanism involving cleavage of an external cyclopropane C-C bond.

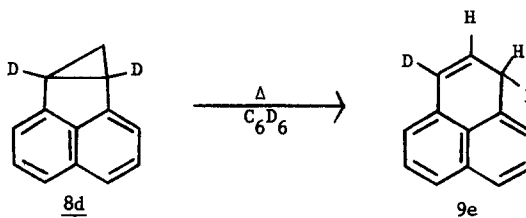


Because one can in principle make a wide variety of D-labeled analogues of 8, it seemed worthwhile to explore in more detail the chemical behavior of singlet and triplet (1)-1,8-NQM (7). Furthermore, because quenching of 3 with O_2 proved so useful in understanding the behavior of 3,^{11,14} it seemed worthwhile to investigate the behavior of the spin states of 7 in the presence of O_2 . It is the purpose of this paper to describe the results of these experiments.

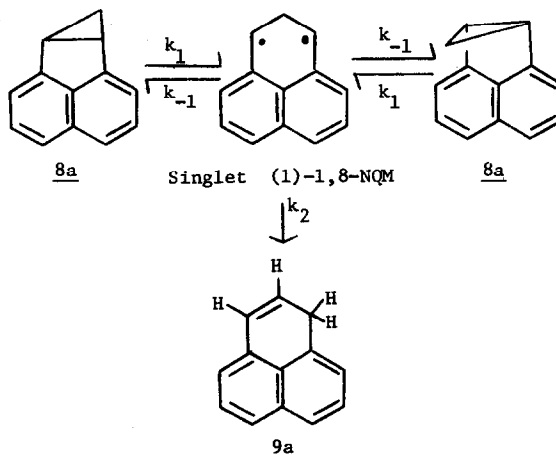
RESULTS AND DISCUSSION

Thermal studies. Is singlet (1)-1,8-NQM (7) an intermediate in the thermal epimerization of 8b and 8c? Mechanisms involving cleavage of the external cyclopropane C-C bond¹⁸ and, less likely, involving no intermediate at all are also possible. The evidence described below, however, is quite convincing that these latter possibilities are not important here.

In addition to the epimerization observed by Roth and Enderer,^{15b} 8a also undergoes in benzene-*d*₆ a slower irreversible isomerization to phenalene (9a). Thermolysis of D labeled 8d in benzene-*d*₆ yields dideuteriophenalene 9e cleanly,¹⁹ demonstrating that this isomerization proceeds by cleavage of the internal cyclopropane C-C bond.

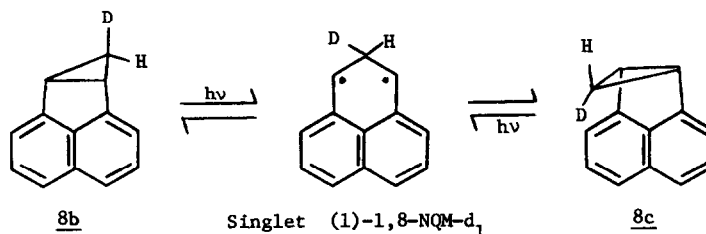


The most economical way of explaining these and Roth and Enderer's results is by having singlet (1)-1,8-NQM (7) be the intermediate in both the epimerization and isomerization reactions as shown below.



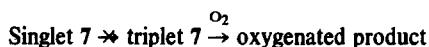
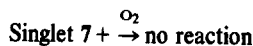
Because there is rate data available for both the epimerization^{15b} and isomerization reactions,¹⁴ one can learn much more about this system. By simple mathematical manipulation of the rate equations and experimental data, it can be shown that Roth's phenomenological rate constant $k_1 + k_{-1}$ and energy of activation (E_a) for the epimerization of **8b** and **8c**, which were determined without any notion of mechanism, correspond exactly to k_1 and E_a (for **8a** → singlet **7**) in the above scheme.²⁰ Furthermore, by use of this k_1 and our experimental data one can determine the ratio $k_{-1} : k_2$, i.e. the rate of ring closure to rate of 1,2-hydrogen shift. In the temperature range in which the kinetics of isomerization of **8a** to **9a** were measured (140–170°), the ratio is approx. 36.

Thus, in fluid solution singlet (1)-1,8-NQM ring closes much more rapidly than it undergoes a 1,2-hydrogen shift. This is in contrast to the results of Michl and



coworkers^{15a} who observed that **7** underwent exclusive 1,2-hydrogen shift in a matrix of high viscosity. As the matrix reaction undoubtedly has the same immediate precursor to product, i.e. singlet (1)-1,8-NQM (**7**), as does the reaction in fluid solution, these results represent a remarkable matrix effect. Perhaps the substantial difference in behavior can be attributed to the reluctance of almost planar **7** to increase the volume of space required for **8a** to fit into the matrix. With the formation of **9a**, however, which is relatively planar, there would be no volume restriction.

Does singlet (1)-1,8-NQM (**7**) react with O₂ in the temperature range of the thermolysis? The answer is no, because thermolysis of **8a** in bromobenzene between 140 and 150°, a temperature range in which both epimerization and isomerization are known to occur, led to no oxygenated products.²¹ Because triplet **7** does react with O₂ (*vide infra*), these "negative" results also demonstrate that the conversion of singlet **7** into ground state triplet **7** is much slower than other chemical processes. These conclusions are exactly analogous to those observed for (2)-1,8-NQM (**3**).



Photochemical studies. Because there was no evidence for the formation of triplet (1)-1,8-NQM (**7**) during the thermolysis of **8a** and **8b**, either in the presence or absence of O₂, it was worth exploring the possibility that one could generate it by photolysis of **8** in fluid solution. Recall that Michl did indeed make it by photolysis of **8a** in a low temperature matrix.^{15a}

Photolysis of **8a** in benzene at room temperature in the absence of O₂ led to its slow irreversible decay. Although NMR analysis of the photolysis residue suggested the presence of phenalene (**9a**), this was not proven as

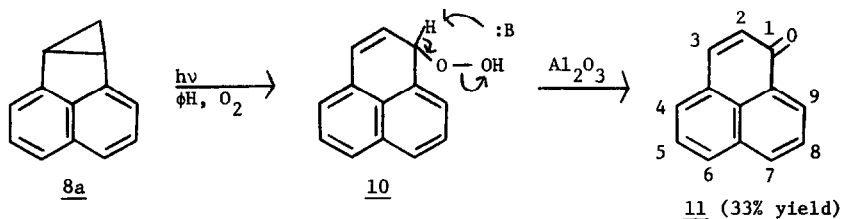
there was too little of it present for isolation and characterization. That phenalene (**9a**) is at least a reasonable product of this reaction was demonstrated by photolysis of **9a**. It also underwent a slow irreversible decay which yielded no characterizable products. Thus phenalene (**9a**) would not have accumulated during the photolysis of **8a**.

Photolysis of *exo*, monodeuteriocyclopropane **8b** in benzene, on the other hand, led to the very rapid epimerization of the D label and, as with **8a**, to a much slower irreversible decay. Because Wirz has demonstrated that photolysis of **8a** in fluid solution does not yield any appreciable amounts of triplet (1)-1,8-NQM (**7**),²³ one can conclude that the photochemical epimerization of **8b** and **8c** occurs thru the intermediacy of singlet (1)-1,8-NQM (**7**).²⁴ Thus, both the thermal and photochemical epimerizations of **8b** and **8c** occur by disrotatory ring opening of the central cyclopropane C-C bond.

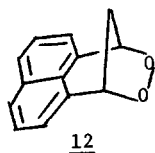
What effect will added O₂ have on the above photoreactions? If O₂ had no effect on the photophysics of **8**, there would be no effect on the chemistry because, as we already have seen, only singlet **7** is produced in the reaction. Of course, any small amounts of triplet **7** generated in the reaction as well as **8a** and any phenalene (**9a**) produced might react. If the presence of O₂ does alter the photophysical properties of **8** such as k_{isc} and Φ ($S_0 \rightarrow T_1$) etc., as might be expected, then larger amounts of triplet (1)-1,8-NQM (**7**) may be produced. As described below, there can be no doubt that triplet **7** is generated during the photolysis of **8** in the presence of O₂ and that it reacts with O₂. It is not clear, however, which of the above scenarios in fact is responsible for the generation of triplet **7**.

Photolysis of **8a** in benzene in the presence of O₂ led to the compound's rapid disappearance.²⁵ Tlc of the photolysis residue on deactivated silica gel (10% ether/ligroine solvent) showed, in addition to **8a**, the presence of a very large spot ($R_f \sim 0.5$) and a slow moving, small yellow one ($R_f \sim 0.2$) belonging to phenalene (**11**); no other spots above the base line were observed. The mass spectrum of the photolysis residue showed a small peak at m/e 198 (**8a** + O₂) and an intense peak at m/e 180 (**8a** + O₂ - H₂O). The ¹H NMR spectrum was not informative as it showed many poorly resolved bands. The IR spectrum, on the other hand, indicated the presence of a OH group. When the photolysis residue was treated with a little alumina, the OH band disappeared and was replaced by the CO stretch of phenalene (**11**). Tlc of the resulting solution now showed a large spot for phenalene, with the original large spot ($R_f \sim 0.5$) having completely disappeared. We take these observations to mean that the major primary photoproduct is the hydroperoxide **10**, which undergoes an elimination reaction in the presence of alumina to yield phenalene (**11**).

Interestingly, there is no evidence from the above results for the presence of the cyclic peroxide **12**. If it



were produced in the photoreaction, however, it almost certainly would undergo a secondary photoreaction, perhaps to yield **10** or a polymer.²⁶ Much polymeric material is produced in the reaction because the yield of phenalene, the only isolated product, is always less than 50%.



Photolysis of **8b** in benzene in the presence of O_2 led, as before, to the rapid epimerization of the D label and to a slower irreversible reaction which, in this case, yielded



phenalene in 21% yield after chromatography of the photolysis residue on alumina. Even though the mass spectrum of the ketone revealed the presence of D (29.3% d_0 , 70.7% d_1), a very careful analysis of the compound's 1H NMR spectrum²⁷ in $CDCl_3$ and CF_3COOH revealed that the label was largely spread out over the entire ring system; notably absent was any excess D at C-2 on **11**.

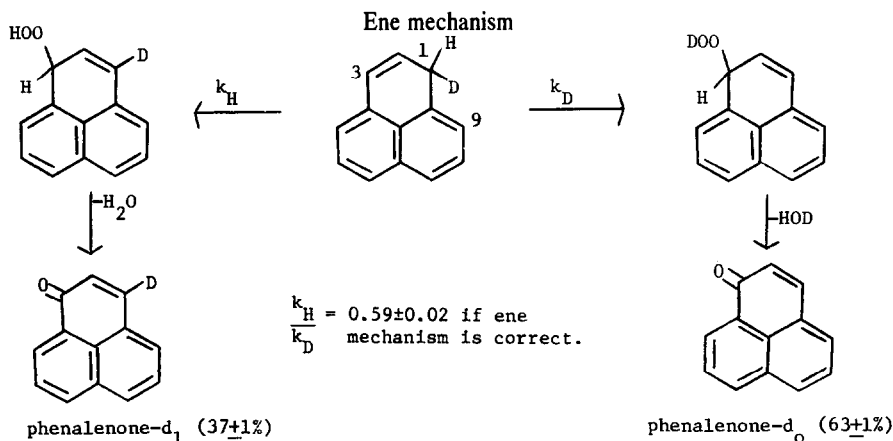
One can conclude from these results that a large fraction of singlet **7** is being generated in the presence of O_2 , either by the ring opening of the singlet excited state of **8** (8^{1*}) and/or indirectly by the route: $8^{3*} \rightarrow$ triplet **7** \rightarrow singlet **7**. One can also conclude that the singlet and triplet excited states of **8** do not react directly with O_2 . We can find no precedence in the literature for a com-

parable reaction. Even more revealing is the fact that most schemes which convert $8^* + O_2$ into **10** (and/or **12**) directly leave a substantial amount of D at C-2 on **10** and ultimately on **11**. This randomization of label is also significant in another way because, if triplet **7** and/or phenalene react with O_2 , they do so in a way that randomizes the label. In fact, is triplet **7** and/or phenalene (**9**) generated in the above reaction and, if so, which of them reacts with O_2 ? The experiments described below address these questions.

Photolysis of phenalene (**9a**) in benzene in the presence of O_2 was qualitatively similar to that of **8a**, with phenalene (**11**) being produced in 41% yield after chromatography of the photolysis residue on alumina. Thus phenalene could be the source of the phenalene which is produced by photolysis of **8a** in benzene/ O_2 .

Irradiation of phenalene- d_1 (**9b**) under the same conditions²⁸ gave phenalene which, by mass spectrometry, was $63 \pm 1\%$ d_0 and $37 \pm 1\%$ d_1 . The 1H NMR spectrum revealed that the D label was not preferentially located at any given carbon. It should be noted that when run to partial conversion, there was no scrambling or loss of D in the recovered phenalene.

How is one to interpret these results? There appear to be only two reasonable interpretations. The first involves the reaction of the excited state(s) of phenalene- d_1 (**9b**) with O_2 by a mechanism equivalent to an ene reaction in which one oxygen atom of O_2 abstracts an H or a D atom from C-1 while the other O atom simultaneously forms a bond to C-3. The hydroperoxides which are formed by the ene reaction would then yield phenalene- d_1 and phenalene- d_0 on treatment with alumina. This inter-



pretation cannot be correct because it would leave the D label exclusively at C-3 of phenalene-d₁. This would have been easily detected experimentally and was not. A similar ene mechanism utilizing C-9 of phenalene-d₁ (**9b**) can be discounted for the same reason, i.e. it would leave the label exclusively at C-9 on phenalene-d₁ which, of course, was not observed.

The more acceptable interpretation requires that **9b*** react with O₂ to yield the phenalenyl radical (d₀ and d₁) and the hydroperoxy radical (d₁ and d₀) which collapses to give 1-hydroperoxyphenalene (10-d₀ and d₁). Because the phenalenyl radical is of high symmetry, the reaction of ·OOH(D) and the phenalenyl radical should occur randomly at the six equivalent corner positions of the organic radical. This will ensure that the D label is not localized at any position on phenalene.²⁹ Analysis of this mechanistic scheme, which is shown below, yields the isotope effect (k_H/k_D) = 0.80 ± 0.04.³⁰

The above results are significant for two reasons. First, it proves that if phenalene were produced in the photoreaction of **8** in benzene/O₂, it would undergo a secondary photoreaction to yield 1-hydroperoxyphenalene (and phenalene). Second, regardless of mechanism, if phenalene-d₁ (**9b**) is produced in the photoisomerization of a deuterated cyclopropane **8**, it will behave in an identical manner to that of the independently made material.

Let us consider the hypothetical behavior of the dideuteriocyclopropane **8d**. If the molecule were to ring open and undergo a 1,2-hydrogen shift, this would yield the phenalene **9e**. If one is willing, for the moment, to neglect the D label at C-3, **9e*** will react with O₂ in an analogous manner to that of **8b**. The D at C-3 could, of course, alter the amount of H and D abstracted by O₂ at C-1. This effect should be negligible, however, because the D at C-3 is common to both hydrogen and D ab-

Abstraction recombination mechanism

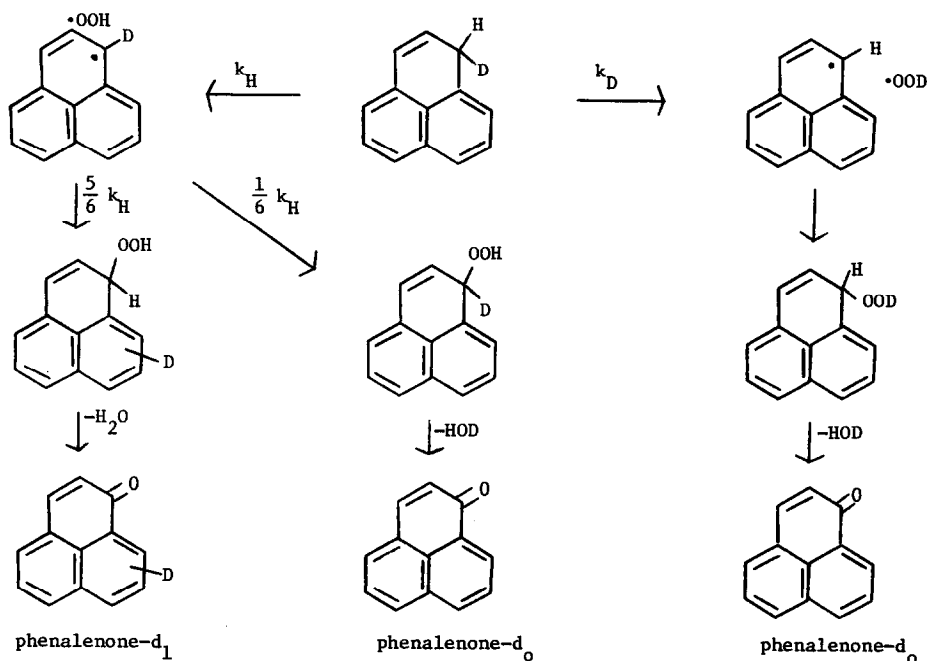
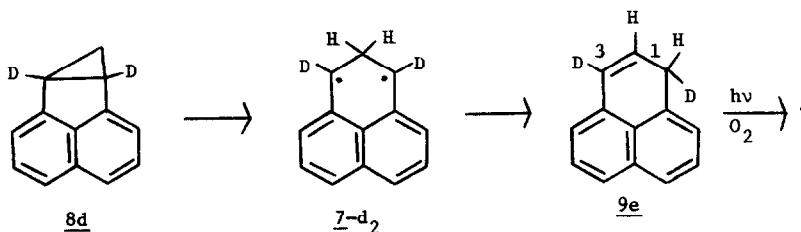


Table 1. Reaction of **9e** and triplet **7-d₂** with O₂; predictions

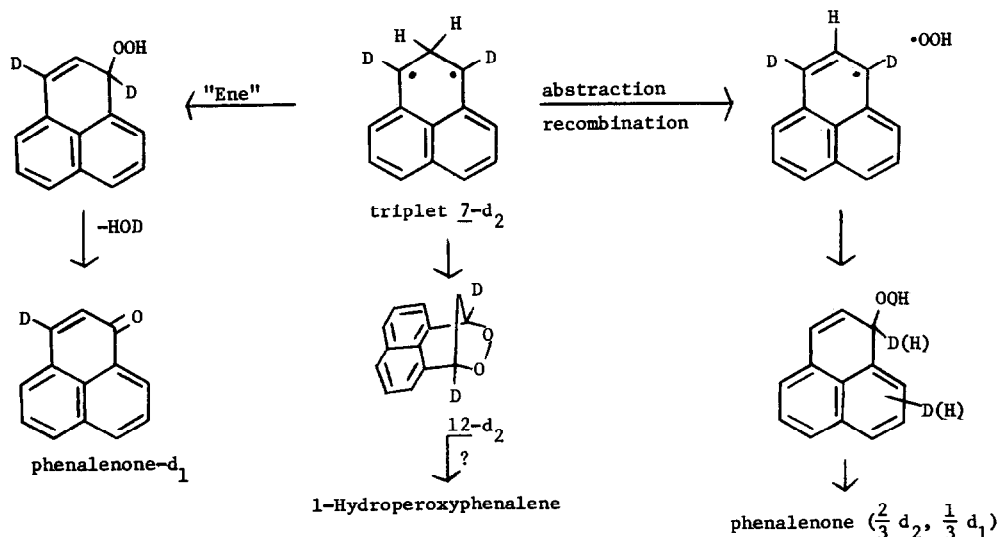
Reactant	Mechanism	d ₀	d ₁	d ₂
Phenalene-d ₁ (9b)	A.R. ^a ($\frac{k_H}{k_D} = 0.8$)	9.3	61.1	29.6
9b	A.R. ^a ($\frac{k_H}{k_D} = 4$)	3.3	43.3	53.3
9b	A.R. ^a ($\frac{k_H}{k_D} = 0.25$)	13.3	73.3	13.3
9b	Ene to C-3	0	100	0
9b	Ene to C-9	0	0	100
Triplet 7-d₂	A.R. ^a	0	33.3	66.7
Triplet 7-d₂	"Ene"	0	100	0
Triplet 7-d₂	Via Peroxide 12-d₂	Difficult to Assess ^b		

a) A.R. - Abstraction Recombination; b) There are several mechanisms by which the cyclic peroxide can be converted into the hydroperoxide.

straction at C-1.³² Thus, the percent of phenalene-*d*₂, -*d*₁, and *d*₀ produced from phenalene generated in this reaction can be predicted from the results obtained for the photolysis of phenalene-*d*₁ (**8b**). (The predictions are shown in Table 1 with (*k_H/k_D*) values of 0.8, 0.25 and 4. The value of 0.8 was found for **8b**.)



If triplet **7-d**₂ were also produced in the photoreaction of **8d**, it could also react with O₂ by an abstraction recombination mechanism, an "ene" mechanism, and also via the cyclic peroxide **12-d**₂ as shown below. The predictions for these hypothetical mechanisms are also shown in Table 1.



recombination mechanism of phenalene plus O₂ will duplicate the experimental results. This is not the case. Furthermore, the experimental results do not yield an internally consistent isotope effect for this mechanism.³⁴ Thus, because the cyclopropane **8** excited state and singlet (1)-1,8-NQM (**7**) do not react with O₂ and

phenalene and triplet **7** are the only other reasonable sources of the hydroperoxide, it follows from these results that they both are sources of this compound when **8** is photolyzed in benzene/O₂. What is unclear, however, is whether triplet **7** reacts with O₂ by an abstraction recombination mechanism or concertedly to produce the

As can be seen in Table 1, one can determine in principle if phenalene or triplet **7** or an admixture of both is responsible for the hydroperoxide production when **8d** is irradiated in benzene/O₂. What in fact are the results?

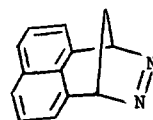
When **8d** is irradiated in benzene/O₂ and the photolysis residue chromatographed on alumina, the resulting phenalene gave an ¹H NMR spectrum in which there was no evidence for excess D at any C. These results plus those obtained from the photolysis of **8b** in benzene/O₂ rule out a concerted mechanism involving exclusively phenalene or triplet **7**. Of course, the reaction of phenalene with O₂ had already been shown to be a stepwise process.

Mass spectrometry of the phenalene yielded the following deuterium distribution: 7.4 ± 0.3% *d*₀, 47.9 ± 0.6% *d*₁, and 44.7 ± 0.9% *d*₂.³³ These data are not consistent with any single species yielding 1-hydroperoxyphenalene (and phenalene), most notably for phenalene whose mechanism for hydroperoxide production is known. It could be argued that by proper adjustment of the isotope effect (*k_H/k_D*) that the predicted D distribution on phenalene derived for the abstraction

cyclic peroxide **12**, which in turn yields the hydroperoxide in a secondary photoreaction.

CONCLUDING REMARKS

Several interesting things have been learned from this study. Suffice it to say that it has been demonstrated that singlet (1)-1,8-NQM (**7**) is generated on thermolysis of **8** and that it neither reacts with O₂ nor undergoes intersystem crossing to ground state triplet (1)-1,8-NQM (**7**) for, if it had, the triplet would have reacted with O₂ by an as yet unknown mechanism. What would be desirable to have in hand in order to continue these studies are the cyclic peroxide **12** and especially the azo compound **13**. Then one could look at the photochemical decomposition of **12** and one could generate **7** under



conditions where the photoproducts don't absorb light. Unfortunately, the syntheses of these compounds have to date proven elusive.

Finally, if one extrapolates Michl's kinetic data for the decay of triplet 7 in a low temperature matrix to room temperature, an admittedly risky endeavor, one will deduce that 7's lifetime is much longer than that of triplet 1 and 3 at the same temperature. It should be possible to trap triplet 7 with diylphiles other than O₂ at room temperature.⁴⁰

EXPERIMENTAL

General comments. Spectra were recorded on the following spectrometers—NMR: Varian T-60 and HA-100 and Nicolet TT14 spectrometers; ms: Hewlett-Packard 5980A gas chromatograph mass spectrometer; IR: Perkin-Elmer 257 grating spectrophotometer; and ESR: Varian E-109 spectrometer. M.ps were obtained using a Thomas-Hoover capillary m.p. apparatus and are uncorrected. Chromatography was performed on alumina using ligroine/ether as the eluant.

Photolyses. The light source for all photolyses was a medium-pressure mercury vapor Hanovia lamp. Samples to be photolyzed at room temp. without light filtration were fastened directly to the cooling jacket of the lamp. Degassed samples were photolyzed in NMR tubes which had been sealed after three "freeze-pump-thaw" cycles. Solns of samples to be photolyzed in the presence of O₂ were placed in pyrex test tubes into which the gas was bubbled directly from its cylinder. 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.

Thermolyses. Most thermolyses were conducted in an oil bath thermostatted at the desired temp., using a temp. regulator built in the department's electronics shop. Degassed samples were thermalized in NMR tubes which had been sealed after three "freeze-pump-thaw" cycles. Solns of samples to be thermalized in the presence of O₂ were placed in test tubes into which the gas was bubbled directly from its cylinder.

Kinetics. A soln of the 8a was prepared in benzene-d₆ containing a small amount of TMS to be used as an internal standard. The soln 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°. 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° for a total of 4.5 hr and at 170° for a total of 4 hr, respectively. The data were analyzed by the least squares computer program given in The Chemist's Companion,³⁵ modified to calculate error limits and activation parameters. These experiments yield the following phenomenological activation parameters: E_a = 34.7 ± 2.1 kcal/mol and A = 10^{13.2±2.2} s⁻¹.

Phenalene (11). This material was prepared by a modification of the procedure of Watson *et al.*⁵

To 3 l of anhyd. ether were added 100 g (2.1 mol) of a NaH oil dispersion (50% by weight hydride), 3 ml EtOH, 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 water was added to the flask to dissolve the solid. The aqueous solution was washed with three 500-ml portions ether and then acidified with 200 ml con. HCl, causing precipitation of a white solid. The solid was extracted into 1 l of ether, which was dried with MgSO₄ and the solvent removed to give a red oily residue. This residue was diluted to 1 l with CCl₄ and added dropwise to 1 l of a vigorously stirred 80% H₂SO₄, cooled in an ice-water bath.

Following the addition, 400-ml portions of the soln were each treated as follows. The aliquot was added to 1.5 l of water and 500 ml CCl₄. The organic phase was collected, and the aqueous phase was twice more extracted with 500 ml portions CCl₄. The organic extractions were combined, dried with MgSO₄, 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 phenalene. This material was used without further purification.

Phenalene (9a). This material was prepared from 11 by the procedure of Boudjouk and Johnson.³⁶

Phenalene-d₁ (9b). Phenalene (1 g, 6 mmol) was dissolved in 300 ml anhyd. ether. To this soln was added under N₂ a slight excess of a soln of n-BuLi in hexane. The resulting, intensely red soln was quenched with a soln of 0.7 ml of 38% DCl/D₂O diluted with some D₂O. The ether was washed with H₂O, dried and removed *in vacuo* yielding phenalene-d₁: NMR (CCl₄) δ 6.90 (m, 6H, naphthalene), 6.31 (d, 1H, J = 10.0 Hz, vinyl), 5.61 (dd, 1H, J = 10.0, 4.0 Hz, vinyl), and 3.65 (br s, 1H, vinyl methylene H). Mass spectrometry was not attempted on this material as phenalene gives an intense M-1 peak even at low ionization voltage.

Naphthocyclopropane (8a). This material was prepared by the general method of Kawabata *et al.*³⁷ for making cyclopropanes from alkenes.

To 50 ml benzene were added 610 mg (4 mmol) acenaphthylene, 1.0 ml (39 mmol) of methylene iodide, 1.14 g Cu powder, and 0.05 g I₂. 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% AgNO₃ alumina column. Elution with 5% ether-95% ligroin gave 290 mg (44%) cyclopropane: m.p. 115.0-116.0° (lit.³⁸ 115-116°); NMR (CCl₄) δ 7.14-7.84 (m, 6H, naphthalene), 2.89 (dd, 2H, J = 4.0, 8.0 Hz, benzylic), 1.40 (dt, 1H, J = 4.0, 8.0 Hz, exo), 0.71 (dt, 1H, J = 4.0, 4.0 Hz, endo).

Naphthocyclopropane-d₁ (8b). This was prepared by the method of Wittig *et al.*,³⁸ modified by inclusion of quinone (1% by weight) in the reaction of acenaphthylene and ethyl diazoacetate and trapping the isocyanate with *tert*-BuOH.

Naphthocyclopropane-d₂ (8d). This was prepared from acenaphthylene-d₂ as described elsewhere³⁹ and modified by running the cyclopropanation according to the procedure described above for 8a. ¹H NMR analysis revealed no residual hydrogen at the benzylic positions. Mass spectrometry was not attempted because 8a showed a prominent M-1 peak even at low ionization voltage. Mass spectrometry on acenaphthylene-d₂ did reveal a very small amount of d₁ and d₀ component. These contributions certainly will carry over to 8d. No corrections were reported in Table 1 for the various predicted reactions; the numbers are altered only slightly and in no way change our conclusions.

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REFERENCES AND NOTES

- 1,8-NQM refers to 1,8-naphthoquinodimethane. The (n) in front of 1,8-NQM indicates the number of methylene groups linking the two diyl carbons. The parent species (1) has no methylenes linking the two diyl carbons and is thus called (0)-1,8-NQM.
- R. M. Pagni and C. R. Watson, Jr., *J. Am. Chem. Soc.* **96**, 2291 (1974).
- C. A. Coulson and A. Streitwieser, Jr., *Dictionary of π -Electron Calculations* p. 112. Freeman, San Francisco (1965).
- R. M. Pagni and C. R. Watson, *Tetrahedron Letters* **59** (1973);
- I. Murata and K. Nakasuji, *Ibid.* **53** (1973).
- C. R. Watson, Jr., R. M. Pagni, J. R. Dodd and J. E. Bloor, *J. Am. Chem. Soc.* **98**, 2551 (1976) and refs cited.
- Small amounts of dimeric products have since been found in the steady state photolytic reactions. The amounts of these

dimers increase when the reaction is run with a flash lamp or with a laser. J. Wirz, unpublished results.

⁷Photolysis of **4a** in MeOH at 20° yields **5**:**6** = 6.7, while at -77° the ratio is greater than 49.⁵

⁸Obviously **5** and **6** are each formed in a separate step, but from the same immediate precursor.

⁹The ratio **5** : **6** was quite different here than observed in fluid solution,⁵ because **3** undergoes a photolytic reaction to give **6**.¹¹

¹⁰The difficulty in performing the Curie law study around 77K can be attributed to the difficulty in correcting for the slow irreversible decay (to **5** and **6**) under these conditions.

¹¹M. Gisin, E. Rommel, J. Wirz, M. N. Burnett and R. M. Pagni, *J. Am. Chem. Soc.* **101**, 2216 (1979).

¹²This work¹¹ and a recent time resolved ESR study¹³ show that **3** is formed within 10⁻⁷ s after photolysis.

¹³W. P. Chisholm, S. I. Weissman, M. N. Burnett and R. M. Pagni, *J. Am. Chem. Soc.* **102**, 7103 (1980).

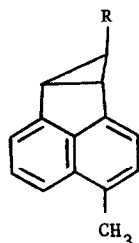
¹⁴M. N. Burnett, Ph.D. Dissertation, University of Tennessee, 1979.

^{15a}J.-F. Muller, D. Muller, H. J. Dewey and J. Michl, *J. Am. Chem. Soc.*, **100**, 1629 (1978); ^bW. R. Roth and K. Enderer, *Liebigs Ann. Chem.* **730**, 82 (1969).

¹⁶Work on the parent (0)-1,8-NQM (**1**) has also been reported, but will not be discussed here. See: ^aM. Gisin and J. Wirz, *Helv. Chim. Acta*, **59**, 2273 (1976); ^bR. M. Pagni, M. N. Burnett and J. R. Dodd, *J. Am. Chem. Soc.* **99**, 1972 (1977); ^cRef. 14; ^dM. Platz, *J. Am. Chem. Soc.* **101**, 3398 (1979); ^eM. Platz, *Ibid.* **102**, 1192 (1980).

¹⁷J. Michl, personal communication.

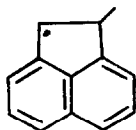
¹⁸One could distinguish whether the epimerization proceeds by internal or external cleavage by comparing the rate of racemization of optically active **i** with the rate of epimerization of optically inactive **ii**.



i) R=H, **ii**) R=D

¹⁹This reaction must be watched very carefully because phenalenes undergo hydrogen shifts in this temp. range.

^{20a}The procedure for relating the rate constants can be found in Ref. 14. ^bAnother factor which favors **7** as an intermediate in these reactions over something like **iii** is the calculated (by Benson's method^{20c}) changes in enthalpy for the reactions which form them. It is found that $\Delta H_f^0(\mathbf{7}) - \Delta H_f^0(\mathbf{8a}) \approx 25$ kcal/mole, while $\Delta H_f^0(\mathbf{iii}) - \Delta H_f^0(\mathbf{8a}) \approx 38$ kcal/mole. The energy of activation determined by Roth and Enderer,^{15b} which is associated with the conversion of **8a** into **7** in our scheme or into **iii** in a similar scheme, is 35.0 ± 0.5 kcal/mole. Thus **iii** could not readily be formed from **8a** thermally. ^cS. W. Benson, *Thermochemical Kinetics*, 2nd Edn. Wiley, New York (1976).



iii

²¹One could argue that the solubility of O₂ is too low for it to react with singlet **7**. This is wrong. Although the solubility of O₂ in bromobenzene in this temp. range is not known, an extensive compilation of solubility data²² suggests that the solubility isn't appreciably different than that for benzene at room temp. One could also argue that singlet **7** is too short lived for it to react

with O₂. This also isn't likely. Consideration of the experimental and thermochemical data suggests that the lifetime of singlet **7** is appreciably larger than 10⁻¹⁰ s.

²²E. Wilhelm and R. Bating, *Chem. Rev.* **73**, 1 (1973).

²³Jakob Wirz, personal communication.

²⁴As in the thermal reaction, the epimerization could occur via cleavage of the external cyclopropane C-C bond. In our judgment this is unlikely as we have never seen any evidence for it in our extensive studies of **8a** and its deuterio derivatives.

²⁵ESR spectra were taken periodically during the photolysis. Only once was the phenalenyl radical detected and only barely at the limits of detection of the spectrometer.

²⁶The hydroperoxide **10** could also be photoactive.

²⁷H. Prinzbach, V. Freudenberger and U. Scheidegger, *Helv. Chim. Acta* **50**, 1087 (1967).

²⁸Irradiation to partial conversion demonstrated that phenalene-d₁ maintained its integrity. There was no evidence for H or D scrambling.

²⁹It is interesting to note that the ene mechanism will give identical results to the abstraction recombination mechanism if the hydroperoxides in the former case randomize the OOH group either during the reaction or on workup.

³⁰It is plausible that ¹O₂ is being generated in the photoreaction and that it then reacts with ground state phenalene-d₁. This mechanism cannot be correct for it yields a product isotope effect (0.59 or 0.80) totally out of line with literature precedent.³¹ To check further on this point we have reacted ¹O₂ with phenalene-d₀ and d₁. The 1-hydroperoxyphenalene is also produced here. One gets the reasonable³¹ isotope effect (k_H/k_D) = 1.05 if the ene mechanism operates and 1.6 if the abstraction recombination mechanism operates. The latter mechanism amazingly is more likely because the ¹H NMR analysis of the phenalene shows that the D label is randomized. These experiments are continuing and will be reported in detail elsewhere.

³¹L. M. Stephenson, M. J. Grdina and M. Orfanopoulos, *Acc. Chem. Res.* **13**, 419 (1980) and refs cited.

³²It is not known whether the singlet or triplet excited states of phenalene react with O₂. If both excited states of phenalene-d₀ react, the presence of D at C-3 could be a problem because the relative amounts of singlet and triplet excited states may change.

³³These values are the results of two separate experiments in which the M⁺ and M⁺-CO peaks were analyzed in each case.

³⁴One can derive the isotope effect (k_H/k_D) by solution of the following three simultaneous equations. Because there are two unknowns, k_H and k_D, and three equations, one can calculate k_H/k_D in three different ways. If phenalene were the only source of the hydroperoxide and it reacted with O₂ by a single mechanism, the equations would be internally consistent and yield the same k_H/k_D. In fact one calculates (k_H/k_D) = 0.74, 1.51 and 2.19 from these equations.

$$\begin{aligned} 0 k_H + \frac{1}{6} k_D &= 0.074 && \text{Production of } d_0 \\ \frac{1}{3} k_H + \frac{5}{6} k_D &= 0.479 && \text{Production of } d_1 \\ \frac{2}{3} k_H + 0 k_D &= 0.447 && \text{Production of } d_2 \end{aligned}$$

Here k_H and k_D represent the relative amount of H and D abstraction at C-1 of **9e** by O₂.

³⁵A. J. Gordon and R. A. Ford, *The Chemist's Companion*, pp. 488-491. Wiley, New York (1972).

³⁶P. Boudjouk and P. D. Johnson, *J. Org. Chem.* **43**, 3979 (1978).

³⁷N. Kawabata, M. Naka and S. Yamashita, *J. Am. Chem. Soc.* **98**, 2676 (1976).

³⁸G. Wittig, V. Rautenstrauch and F. Wingler, *Tetrahedron Suppl.* **7**, 189 (1966).

³⁹J. R. Dodd, R. M. Pagni and C. R. Watson, Jr., *J. Org. Chem.* **46**, 1688 (1981).

⁴⁰The two referees of this paper have brought up the following pertinent questions about singlet (1)-1,8-NQM (**7**). First, is it an

actual species? Second, if it is a true species, is it an intermediate in the thermal isomerization of **8**? Third, is it produced from triplet **7**, i.e. triplet **7** → singlet **7**, during the photolysis of **8**, either in fluid solution or in low temp. glassy matrices? As noted several places in the text, the answers to these three questions are not known unequivocally. We choose to answer all of these questions in the affirmative for the following reasons.

First, the existence of singlet **7** is quite reasonable because the existence of the structurally related singlet **3** has been demonstrated. Second, the intermediacy of singlet **7** during the thermolysis of **8** is also quite reasonable. In addition to all the arguments presented in the text, one can also mention the following argument. The calculated $\Delta H_f(7)$,^{20c} determined either directly or by removal of two benzylic hydrogen atoms

from phenalane, is 6 to 11 kcal/mol below $\Delta H_f(8) + \Delta H^\ddagger$ for the thermolysis which leads from **8** to singlet **7**. In other words, these calculations not only put singlet **7** into a potential energy well but also give singlet **7** a ΔH_f which is compatible with its existence in thermal isomerization of **8**. Third, the existence of the reaction triplet **7** → singlet **7** is, again, quite reasonable because, for the closely related ethylene-bridged 1,8-NQM (**3**), the corresponding reaction has been demonstrated.

We must emphasize that, although we believe that singlet **7** plays an integral part in the chemistry described in the text, none of the above questions concerning singlet **7** has been answered unambiguously. The answers to these very important questions await further experimentation.