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1,4-Perinaphthadiyl. Singlet- and Triplet-State Reactivity of a Conjugated Hydrocarbon Biradical

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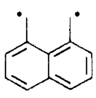
Abstract: 1,4-Perinaphthadiyl (b) was generated from the azo precursor **1** by thermal elimination of nitrogen as well as by direct and sensitized photolysis. The biradical was persistent but light sensitive at low temperature in the triplet ground state (^{3}b) and was characterized by optical and ESR spectroscopy; kinetic and spectrographic flash photolysis was used to monitor ^{3}b at room temperature as a transient intermediate yielding naphthocyclobutane (**2**), divinylnaphthalene (**3**), and dimers (**9**, **10**). The lifetime of ^{3}b was reduced from $\tau = 0.2$ ms in degassed solution to 0.2 μs in air-saturated solution, and as a result, peroxides (**4**, **6**) were formed at the expense of the hydrocarbon products. However, the dependence of the peroxide yield on oxygen pressure required that a second intermediate also interacted with oxygen. This was identified as the singlet state of b undergoing catalyzed intersystem-crossing (ISC) upon diffusional encounter with triplet oxygen; its lifetime at 300 K was estimated as 1 ns, and the energy difference between ^{1}b and ^{3}b as 5 kcal/mol. The efficiency of spontaneous ISC from ^{1}b to ^{3}b was found to increase with decreasing temperature, and the yields of the different final products (**2–4**, **6**, **9**, **10**) were strongly influenced by the conditions chosen for the formation of the biradical. The chemical properties of b are strikingly different from those of the related 1,3-perinaphthadiyls c and d due to the much shorter intrinsic lifetime of ^{1}c and ^{1}d.

The π,π biradical 1,8-naphthoquinodimethane (a) and several of its derivatives are persistent in the triplet state at or below 77 K in rigid glassy solutions and have been thoroughly characterized by a number of spectroscopic methods,[1-9] but little is known about their reactivity in solution, and there are no experimental data about the lowest singlet state of these biradicals. We have sought to obtain such information by combining low-temperature and time-resolved spectroscopy with quantitative product analyses. Several reasons led us to choose 1,4-perinaphthadiyl (7,8,9,10-tetrahydrocyclohepta[*de*]naphthalene-7,10-diyl, b) for this work: naphthoquinodimethane biradicals are well suited for optical detection and hence for flash photolysis; several pathways (pyrolysis, direct photolysis, triplet sensitization) are available for the formation of b from its azo precursor 1,4-dihydro-1,4-ethanonaphtho[*de*][1,2]diazepine (**1**), which is also available with a stereochemical label (**1**-d_2); finally, we were interested in comparing the reactivity of the tetramethylene biradical b with that of the related trimethylene biradical 1,3-perinaphthadiyl (c).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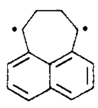
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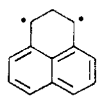
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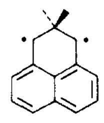
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Previous studies of c[10] and of its 2,2-dimethyl derivative d[8] led to the conclusion that the collapse of these singlet 1,3 biradicals by ring closure or 1,2 H shift is too fast ($\geq 10^{12}$ s^{-1})[8] to allow for any intersystem-crossing (ISC) to the long-lived triplet ground state or for intermolecular trapping reactions. The results presented here indicate that, in contrast, singlet 1,4-perinaphthadiyl (^{1}b) is a true intermediate that decays by several competing decay paths.

The trapping of biradicals by molecular oxygen provides a useful diagnostic tool to determine the yield and lifetime of these reactive intermediates.[11,12] Is it safe to assume that the oxidation products are formed exclusively by the trapping of triplet biradicals, or do we need to consider the reaction of singlet biradicals with triplet oxygen as a real possibility? One may be tempted to dismiss the second alternative on the premises that, first, singlet biradical lifetimes are too short to allow for diffusional encounters with oxygen and that, second, peroxide formation from singlet biradicals with triplet oxygen is inhibited by the spin barrier. Actually, neither of these arguments is well-founded. We report our evidence for the efficient trapping of the singlet biradical ^{1}b by molecular oxygen. The method should be of general value to obtain indirect evidence for the existence of singlet biradical intermediates with a lifetime of at least picoseconds.

Experimental Section

General Procedures and Instrumentation. Experimental procedures for the photochemical and thermal nitrogen elimination from the azo precursor 1,4-dihydro-1,4-ethanonaphtho[*de*][1,2]diazepine (**1**) in degassed solutions and the yields of the resulting hydrocarbons 6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (naphthocyclobutane, **2**) and 1,8-diethenylnaphthalene (**3**) as a function of temperature have been reported previously.[2b] The methods used to trap the biradical intermediates and

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to determine the ensuing product distributions are described below. The results of all these experiments are collected in Table I (see Results).

For preparative photolyses a medium-pressure mercury arc was used as a continuous source of irradiation. When high light powers were desired in order to increase the yield of biradical dimerization products, the samples were flashed repetitively with the output of a 2000-J xenon flash lamp commercially available for photographic purposes. Suitable band-pass or cutoff glass filters were used with both light sources as indicated in the text. Photolyses at −78 °C were conducted by placing the sample tubes in a glass dewar containing a dry ice/acetone bath. Gas pressures were maintained as follows. Degassed samples were photolyzed in glass (often NMR) tubes that had been sealed after three "freeze-pump-thaw" cycles. Solutions to be photolyzed under 1 atm oxygen were placed in open test tubes, and the gas was continuously bubbled through the solution. Photolyses under oxygen pressure were done with Griffin-Worden pressure vessels from Kontes Scientific Glassware.

Most thermolyses were conducted by placing the sample tube in an oil bath equipped with a thermostat. Gas pressures were maintained as described for the photolyses. For the application of gas pressures exceeding 5 atm, the sample was placed into a steel autoclave with external electric heating. With this setup only a very crude temperature control was possible, and the actual sample temperature could not be monitored directly.

Flash spectroscopy of long-lived transient intermediates ($\tau > 50\ \mu s$) was done with an apparatus of conventional design.[13] The excitation flash was produced by an electric discharge (1000 J, 20 μs) through two parallel quartz tubes of 16-cm length and 1-cm diameter, which were kept at a reduced pressure of ca. 6 kPa. The light flash was filtered through suitable cutoff glass filters. Evacuable quartz or glass sample cells of 10-cm length and 2-cm diameter were placed between the discharge tubes. Solute concentrations were chosen to give an absorbance of ca. 0.5 at the excitation wavelengths. Short-lived transients ($20\ \text{ns} < \tau < 100\ \mu s$) were monitored on a laser flash apparatus using the frequency-tripled (353-nm) or quadrupled (265-nm) 20-ns pulses of ca. 50 mJ from a Nd glass laser. The detection system has been described previously;[1d,14a] it allowed for the simultaneous capture of the kinetic trace (at a given wavelength) and of the transient absorption spectrum (at a given time delay after excitation) in digital form and with nanosecond time resolution. The kinetic and spectrographic data were processed by computer.

A solvent mixture known as EPA (diethyl ether/isopentane/ethanol, 5:5:2) was used to obtain rigid glassy solutions for optical spectroscopy at 77 K; the experimental setup has been described.[14a] H NMR spectra are reported as follows: (solvent, magnetic field/MHz), downfield chemical shift δ/ppm vs internal tetramethylsilane (splitting, number of protons, coupling constants, assignment). Only the longest wavelength electronic absorption bands [λ_{max}/nm, ϵ/M^{-1} cm^{-1}] and only the most characteristic infrared bands ($\tilde{\nu}_{max}$/cm^{-1}) and peaks of the mass spectrum (m/z, relative intensity) are reported for compound characterization.

Syntheses. 1,4-Dihydro-1,4-ethanonaphtho[1,8-*de*][1,2]diazepine (1). This compound was prepared by the method of Watson et al.[2b] except that phenalene was prepared from phenalenone by the method of Boudjouk and Johnson[15] and phenalenone was prepared from 1-acetonaphthone by the method of Pagni et al.[10] Chromatographic purification of the product 1 with chloroform on silica gel and slow precipitation induced by adding hot *n*-hexane to a concentrated chloroform solution followed by slow cooling to −20 °C gave pale yellow crystals: mp 123–125 °C (lit.[2b] glassy solid); UV (hexane) 410 nm (ϵ 1380), (acetonitrile) 410, (ϵ 1170), (methanol) 408 (ϵ 1170).

(1α,4α,11*R,12*S**)-1,4-Dihydro-1,4-ethanonaphtho[1,8-*de*][1,2]-diazepine-11,12-d_2 (1-d_2).** Compound 1-d_2 was prepared in the same way as 1, starting from 2,3-dihydro-1,2,3-metheno-1*H*-phenalene-2,10-d_2.[16] Integration of the bridgehead and methylene H NMR peaks showed the compound to be 94% deuteriated (d_2) at the methylene groups.

1*H*,4*H*-1,4-Ethenonaphtho[1,8-*de*][1,2]dioxepin. A solution of 340 mg (1.9 mmol) of cyclohepta[*de*]naphthalene[2b] and 23 mg of *meso*-tetraphenylporphine in 5.5 mL of methylene chloride was photolyzed at −78 °C, while oxygen was bubbled through the solution. After 2 h of irradiation the solvent was removed by a rotary evaporator, and the solid was partly dissolved in methanol leaving the sparingly soluble sensitizer behind. The filtrate was again evaporated and the residue chromatographed on silica gel. Elution with 5% ether in ligroin removed unreacted cyclohepta[*de*]naphthalene, while 10% ether in ligroin eluted the remaining sensitizer. Elution with 20% ether in ligroin afforded 273 mg (68%) of white flakes: mp 134.5–135.5 °C; NMR ($CDCl_3$, 60 MHz) δ 7.07–7.90 (m, 6 H, aromatic), 6.65 (dd, 2 H, J = 3.2, 5.2 Hz, vinyl), 5.46 (dd, 2 H, J = 3.2, 5.2 Hz, bridgehead); UV (95% ethanol) 294 nm (ϵ 5400); MS (70 eV) 210 (4), 178 (100), 152 (43). Anal. Calcd ($C_{14}H_{10}O_2$) C 79.98; H, 4.79. Found: C, 78.42; H, 4.85.

1*H*,4*H*-1,4-Ethanonaphtho[1,8-*de*][1,2]dioxepin (4). Compound 4 was prepared by the general procedure of Adam and Eggelte for the reduction of unsaturated peroxides.[17] To a solution of 160 mg (0.76 mmol) of 1*H*,4*H*-1,4-ethenonaphtho[1,8-*de*][1,2]dioxepin in 20 mL of methylene chloride (distilled from calcium hydride) was added 3.3 g of dipotassium azodicarboxylate.[18] While being stirred under nitrogen, the mixture was cooled to −78 °C, and a solution of 2 mL of glacial acetic acid diluted to 10 mL with methylene chloride was added dropwise. Following the addition, the mixture was returned slowly to room temperature and stirred overnight. The solids present were filtered from the mixture, and the solvent was removed on a rotary evaporator. The residue was chromatographed on silica gel with 6% ether in ligroin. The resulting oil was crystallized from ligroin, giving white needles of 4: mp 88–89 °C; NMR ($CDCl_3$, 90 MHz) δ 7.81 (dd, 2 H, J = 7.9, 1.7 Hz, aromatic peri H), 7.26–7.52 (m, 4 H, aromatic), 5.3–5.4 (m, 2 H, bridgehead), 2.6–2.8 (m, 2 H, methylene), 1.94–2.15 (m, 2 H, methylene); UV (95% ethanol) 286 nm (ϵ 6900); MS (25 eV) 212 (83), 180 (48), 165 (100). Anal. ($C_{14}H_{12}O_2$) C, H.

Head-to-Head Dimer 5 of the Biradical b. The photodimer of cyclohepta[*de*]naphthalene, 7,8,15,16-tetrahydro-7,16:8,15-diethenocyclodeca[1,2,3-*de*:6,7,8-*d′e′*]dinaphthalene (120 mg),[19] was dissolved in 100 mL of chloroform and reduced with hydrogen in the presence of PtO_2, until the starting material had reacted completely (TLC analysis on silica gel, eluting with 10% benzene in CCl_4). The solvent was evaporated, and the solid residue was recrystallized twice from methylene chloride, yielding colorless crystals (90 mg) of the head-to-head dimer 7,8,15,16-tetrahydro-7,16:8,15-diethanocyclodeca[1,2,3-*de*:6,7,8-*d′e′*]dinaphthalene (5): mp 280–281 °C; NMR ($CDCl_3$, 90 MHz) δ 7.20 (dd, 4 H, J = 7.8, 1.8 Hz, aromatic peri H), 6.70–6.95 (m, 8 H, aromatic), 4.08 (br s, 4 H, bridgehead), 2.8 (br m, 4 H, methylene) 2.4 (br m, 4 H, methylene); MS (70 eV) 360 (M^+, 4), 181 (50), 180 (20), 179 (100); UV (hexane) 295 nm ($\epsilon \cong 10^4$, slightly soluble).

Photolyses and Thermolyses. Thermal and Photochemical Stability of the Products. Control experiments showed that the hydrocarbon products 2 and 3 were stable under all the photolysis and pyrolysis conditions used.

The cyclic peroxide 4 was also inert to the photochemical reaction conditions at ambient temperature ($\lambda > 380$ nm, C_6D_6) but reacted slowly under the conditions used at −78 °C ($\lambda > 340$ nm); prolonged irradiation of 4 led to the formation of an unidentified ketone: NMR (C_6D_6, 60 MHz) δ 8.5 (dd), 7.0–7.7 (m), 2.9 (s); IR (C_6D_6) 1690 cm^{-1}. Heating a solution of 4 in C_6D_6 to 150 °C for 24 h led to no decomposition. However, pyrolysis at 180 °C did result in a reaction yielding an unidentified product mixture that gave many poorly resolved H NMR peaks (C_6D_6) different from those observed after photolysis.

The hydroperoxide 6 (vide infra) was stable in methanol and deuteriochloroform at room temperature for extended periods of time but decomposed completely in benzene within less than 12 h. It also decomposed slowly under the low-temperature irradiation conditions ($\lambda > 340$ nm).

Photolysis of 1 at Room Temperature under Oxygen. (a) Benzene, 1 atm O_2 (Table I, Entry 2). Photolysis ($\lambda > 380$ nm) of 1 in reagent-grade benzene (typically 20 mg of 1 in 50 mL of reagent-grade benzene) gave a product mixture that by TLC analysis was found to contain the peroxide 4 in addition to the hydrocarbons 2 and 3. The relative product distribution was determined by 200-MHz H NMR after evaporation of the solvent and dissolution of the residue in C_6D_6. No resonances other than those due to compounds 2–4 were discernible in the spectrum.

(b) Methylcyclohexane, 1 atm O_2 (Table I, Entry 5). After the photolysis of 1 ($\lambda > 380$ nm; 11.5 mg in 90 mL of purified methylcyclohexane), the mixture was worked up and analyzed as described under a. The 200-MHz H NMR spectrum showed some very small unidentified resonances in addition to those of 2–4.

(c) Benzene, 4.6 atm O_2 (Table I, Entry 3). The product distribution was determined by 400-MHz H NMR spectroscopy (C_6D_6). The spec-

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trum was essentially free of peaks not attributable to compounds **2–4**.

(d) Methanol, 1 atm O_2 (Table I, Entry 10). After the photolysis of **1** (λ >380 nm; 11.5 mg in 95 mL of reagent-grade methanol) and solvent removal, a pale yellow oil was obtained that solidified on standing. TLC analysis revealed the presence of one major and two minor unknown components in addition to the known products **2–4**. The large spot was subsequently identified as 7-hydroperoxy-7,8-dihydrocyclohepta[*de*]naphthalene (**6**, vide infra). The product distribution was determined in $CDCl_3$ by 200-MHz H NMR analysis; only a few small peaks remained unassigned.

Photolysis of 1-d_2 at Room Temperature under Oxygen (Table I, Entry 4). The photolysis was performed under conditions identical with those used for **1** in benzene under 1 atm oxygen. The presence of deuterium simplified the H NMR spectra, and it was possible to deduce the product and deuterium distribution from 60-MHz NMR spectra taken before and after chromatographic separation of the products.

Photolysis of 1 at −78 °C under Oxygen. (a) Methanol, 1 atm O_2 (Table I, Entry 11). After the photolysis (λ >340 nm) of 41.2 mg of **1** in 150 mL of reagent-grade methanol, the solution was warmed to room temperature, and the solvent was removed in vacuo. TLC analysis of the resulting pale yellow oil on silica gel with 16% ether in ligroin showed the presence of one major and three minor products; none of the known compounds **1–4** were among these components: IR (CH_2Cl_2) 3500 cm^{-1} (-OOH); H NMR ($CDCl_3$, 60 MHz) δ 7.1–7.9 (m, aromatic), 6.8 (d, J = 12 Hz, vinyl), 6.0 (m, vinyl), 5.4 (m, methine next to OOH), 3.0 (m, methylene), 1.8–2.8 (br m). The resonances at δ 6.8, 6.0, and 3.0 had relative areas of 1:1:2, while the resonance at 5.4 integrated for approximately 2. The peaks at δ 6.8, 6.0, 5.4 (in part), and 3.0 are attributed to 7-hydroperoxy-7,8-dihydrocyclohepta[*de*]naphthalene (**6**) on the basis of the results described below. Assuming that all the components in the mixture were 1,8-disubstituted naphthalenes, greater than 50% of the material was **6**. Other runs analyzed for up to 70% **6**.

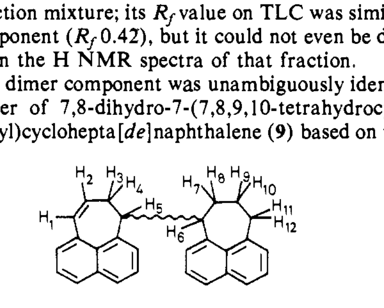
Because the hydroperoxide did not survive column chromatography, the product mixture was reduced with 105 mg of $LiAlH_4$ in 25 mL of ether at room temperature under N_2 for 95 min. After the mixture was quenched with aqueous Na_2SO_4, the ether was separated from the aqueous layer, dried over anhydrous $MgSO_4$, and removed in vacuo. TLC on silica gel with 16% ether in ligroin showed two spots of equal size above R_f 0, both of which moved more slowly than the hydroperoxide. The two components were separated by chromatography on alumina, eluting with ether in ligroin. The first component eluting from the column was vacuum distilled [100 °C (3 mm)] and yielded a colorless oil: MS (25 eV) 196 (M^+), 168 ($M^+ - CH_2CH_2$, base peak); H NMR ($CDCl_3$, 60 MHz) δ 7.55 (d, 2 H, arom.), 7.30 (t, 2 H, arom.), 7.09 (d, 2 H, arom.), 5.33 (m, 2 H, methine), 2.43 (m, 2 H, methylene endo to oxygen), 1.89 (m, 2 H, methylene exo to oxygen). The small amount of this compound could not be induced to crystallize, but it did have an H NMR spectrum identical with that of an authentic sample of 7,8,9,10-tetrahydro-7,10-epoxycyclohepta[*de*]naphthalene (**7**).[20] The second component eluting from the column was also distilled in vacuo [100 °C (3 mm)] and yielded a colorless oil: MS (25 eV) 196 (M^+), 178 ($M^+ - H_2O$), 168, 167 (base peak); H NMR ($CDCl_3$, 60 MHz) δ 7.15–7.92 (m, 6 H, aromatic), 6.83 (d, J = 12 Hz, vinyl next to naphthalene ring), 5.88 (dt, J = 12, 5 Hz, vinyl next to CH_2), 5.16 (m, 1 H, methine), 2.83 (m, 2 H, methylene). TLC analysis on silica gel with 20% ether in ligroin showed one large spot and two tiny trailing spots; further chromatography on silica gel and Florisil did not improve this situation. The H NMR spectrum of this compound is identical with that reported by Meinwald and co-workers for 7,8-dihydrocyclohepta[*d*,*e*]naphthalen-7-ol (**8**).[20,21]

(b) Methylcyclohexane, 1 atm O_2 (Table I, Entry 6). The irradiation (λ >340 nm) of compound **1** (15.6 mg) in 150 mL of purified and distilled methylcyclohexane at −78 °C led to the formation of a large amount of particulate matter. The solution was warmed to room temperature, and the solvent was removed in vacuo without heating. This left a yellow amorphous solid. TLC analysis on silica gel with 12% ether in ligroin showed that the starting material was gone and that no (or very little) hydrocarbon products (**2** and/or **3**) and no cyclic peroxide (**4**) had been formed. H NMR analysis confirmed the absence of **2–4** and revealed the presence of the hydroperoxide **6**.

Preparative Flash Photolysis of 1 in Degassed Methanol. A solution of 300 mg of **1** in 30 mL of degassed spectrograde methanol was photolyzed (λ >340 nm) with 120 flashes until the $n\pi^*$ absorption band of **1**, monitored by a 1-mm quartz cell attached to the sealed vessel, had disappeared completely. After removal of the solvent, the residue was dissolved in a small amount of carbon tetrachloride and chromatographed on silica gel. Ligroin (40–60 °C) eluted the monomer fraction (hydrocarbons **2** and **3**, ca. 200 mg); a second fraction containing mainly dimers and some higher oligomers of b was eluted with ether (ca. 20 mg). TLC (silica gel, CCl_4/hexane, 1:1) and HPLC (reversed phase, methanol/water, 10:1 or silica gel, hexane) analyses of the dimer fraction indicated the presence of one major (TLC, R_f 0.54; ca. 50%) and two minor components (TLC, R_f 0.42 and 0.31; ca. 20% each) in addition to some very minor traces.

Further separation of the components of the dimer fraction proved to be difficult. Repeated chromatography using a commercial silica gel column (Lobar 40–63 μm; Merck), thin-layer chromatography, and fractional sublimation in vacuo at 120–130 °C finally yielded small samples of each component, which were essentially pure by TLC and H NMR standards. Notably, the head-to-head sym dimer **5** was clearly not present in the reaction mixture; its R_f value on TLC was similar to that of the second component (R_f 0.42), but it could not even be detected as a trace impurity in the H NMR spectra of that fraction.

The first major dimer component was unambiguously identified as a single diastereomer of 7,8-dihydro-7-(7,8,9,10-tetrahydrocyclohepta-[*de*]naphthalen-7-yl)cyclohepta[*de*]naphthalene (**9**) based on the following spectroscopic data: MS (75 eV) 360 (M^+, 4), 181 (48), 180 (26), 179 (100); H NMR [($CDCl_3$, 90 MHz with decoupling experiments, 400 MHz with decoupling experiments, 500 MHz). In the 400- and 500-MHz spectra many protons were considerably broadened due to a coalescence phenomenon (presumably ring inversion in the tetrahydrocycloheptene moiety). The 400-MHz spectra were therefore taken at 50 °C, which led to sharp resonances for most protons. The assignments of chemical shifts and coupling constants refer to the structural formula for **9**.] δ 7.67, 7.71, 7.76, 7.80 (each dd, 1 H each, $J \cong 8$, 1 Hz, aromatic peri H), 7.2–7.6 (m, 8 H, aromatic), 6.65 (dd, 1 H, $J_{1,2}$ = 11.5 Hz, $J_{1,4}$ = 3 Hz, vinyl H_1), 5.52 (ddd, 1 H, $J_{1,2}$ = 11.5 Hz, $J_{2,3}$ = 8 Hz, $J_{2,4}$ = 3.5 Hz, vinyl H_2), 4.06 (dd, 1 H, $J_{5,6}$ = 11.5 Hz, $J_{6,7}$ = 5 Hz, bridgehead H_6), 4.01 (ddd, 1 H, $J_{5,6}$ = 11.5 Hz, $J_{3,5} \cong J_{4,5} \cong 2$ Hz, bridgehead H_5), 3.32 (br, 1 H, H_{11}), 3.06 (ddd, 1 H, $J_{11,12}$ = 16 Hz, $J_{8,12}$ = 8 Hz, $J_{10,12}$ = 2 Hz, H_{12}), 2.60 (dddd, 1 H, $J_{3,4}$ = 18 Hz, $J_{2,4}$ = 3.5 Hz, $J_{1,4}$ = 3 Hz, $J_{4,5} \cong 2$ Hz, H_4), 2.24 (br, 1 H, H_3), 1.69 (m, 2 H, H_8 and H_{10}), 1.31 (m, 2 H, H_7 and H_9); UV (hexane) 331 nm ($\epsilon \cong 4000$), 313 ($\epsilon \cong 8000$), 301 ($\epsilon \cong 9000$); fluorescence (hexane, excitation 313 nm) 345 nm (sh), 359 (max), 375 (sh).



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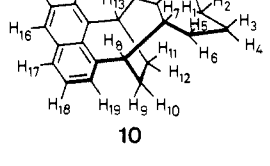
The second dimer (R_f 0.42) proved to be a single stereoisomer of 2,5-naphtho[*def*]-11,13-naphtho[*de*]tricyclo[8.3.2.0^{3,9}]pentadeca-2,4,11,12-tetraene (**10**): MS (70 eV) 361 (M^+ + 1, 28), 360 (M^+, 100), 332 (18), 179 (31), 165 (33); H NMR [($CDCl_3$, 400 MHz) All geminal and vicinal coupling constants of protons on saturated carbons and of ortho and meta coupling constants of aromatic protons were assigned on the basis of decoupling experiments. CD_2Cl_2 was used as a solvent to analyze couplings in the aromatic system. Assignments refer to the structural formula for **10**; the assignments of protons H_{14}–H_{16} may have to be interchanged with H_{19}–H_{17}.] δ 7.69 (dd, 1 H, $J_{17,18}$ = 8 Hz, $J_{17,19}$ = 1 Hz, H_{17}), 7.67 (dd, 1 H, $J_{15,16}$ = 8 Hz, $J_{14,16}$ = 1 Hz, H_{16}), 7.52 (dd, 1 H, $J_{22,23}$ = 8 Hz, $J_{22,24}$ = 1 Hz, H_{22}), 7.49 (d, 1 H, $J_{20,21}$ = 8 Hz, H_{21}), 7.48 (br d, 1 H, $J_{18,19}$ = 8 Hz, H_{19}), 7.36 (dd, 1 H, $J_{17,18}$ = 8 Hz, $J_{18,19}$ = 7 Hz, H_{18}), 7.35 (dd, 1 H, $J_{14,15}$ = 8 Hz, $J_{14,16}$ = 1 Hz, H_{14}), 7.32 (dd, 1 H, $J_{15,16}$ = 8 Hz, $J_{14,15}$ = 8 Hz, H_{15}), 7.24 (d, 1 H, $J_{20,21}$ = 8 Hz, H_{20}), 7.20 (dd, 1 H, $J_{22,23}$ = 8 Hz, $J_{23,24}$ = 7.5 Hz, H_{23}), 7.16 (br d, 1 H, $J_{23,24}$ = 7.5 Hz, $J_{1,24} \cong 1$ Hz, H_{24}), 4.52 (dd, 1 H, $J_{11,13} = J_{12,13}$ = 4 Hz, H_{13}), 4.27 (ddd, 1 H, $J_{6,7}$ = 12 Hz, $J_{7,8}$ = 6 Hz, $J_{7,5}$ = 3 Hz, H_7), 3.73 (ddd, 1 H, $J_{7,8}$ = 6 Hz, $J_{8,9}$ = 5 Hz, $J_{8,10}$ = 4 Hz, H_8), 3.52 (br ddd, 1 H, $J_{1,2}$ = 15 Hz, $J_{1,4}$ = 13 Hz, $J_{1,3}$ = 4 Hz, H_1), 2.83 (ddd, 1 H, $J_{1,2}$ = 15 Hz,



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$J_{2,4}$ = 4 Hz, $J_{2,3}$ = 3 Hz, H_2), 2.49 (dddd, 1 H, $J_{11,12}$ = 14 Hz, $J_{9,11}$ = 8 Hz, $J_{10,11}$ = 5.5 Hz, $J_{11,13}$ = 4 Hz, H_{11}), 2.32 (dddd, 1 H, $J_{11,12}$ = 14 Hz, $J_{10,12}$ = 8 Hz, $J_{9,12}$ = 7 Hz, $J_{12,13}$ = 4 Hz, H_{12}), 2.21 (dddd, 1 H, $J_{9,10}$ = 14 Hz, $J_{9,11}$ = 8 Hz, $J_{8,9}$ = 5 Hz, $J_{9,12}$ = 4 Hz, H_9), 2.15 (dddd, 1 H, $J_{9,10}$ = 14 Hz, $J_{10,12}$ = 8 Hz, $J_{10,11}$ = 5.5 Hz, $J_{8,10}$ = 4 Hz, H_{10}), 1.95 (ddddd, 1 H, $J_{3,5}$ = 14 Hz, $J_{3,4}$ = 8 Hz, $J_{3,6}$ = 7 Hz, $J_{1,3}$ = 4 Hz, $J_{2,3}$ = 3 Hz, H_3), 1.76 (dddd, 1 H, $J_{3,5}$ = 14 Hz, $J_{4,5}$ = 8 Hz, $J_{5,6}$ = 7 Hz, $J_{5,7}$ = 3 Hz, H_5), 1.60 (ddddd, 1 H, $J_{1,4}$ = 13 Hz, $J_{4,6}$ = 11 Hz, $J_{3,4}$ = $J_{4,5}$ = 8 Hz, $J_{2,4}$ = 4 Hz, H_4), 1.15 (dddd, 1 H, $J_{6,7}$ = 12 Hz, $J_{4,6}$ = 11 Hz, $J_{5,6}$ = $J_{3,6}$ = 7 Hz, H_6); UV (hexane) 326 nm ($\epsilon \cong 1000$), 303 (sh, $\epsilon \cong$ 7000), 292 ($\epsilon \cong 9000$), 284 (sh, $\epsilon \cong 8000$); fluorescence (hexane, excitation 313 nm) 355 nm (max).

The third component of the dimer fraction was somewhat unstable to prolonged chromatography and could not be identified: MS 361 (20), 360 (69), 181 (45), 179 (100).

Thermolysis of 1 under Oxygen. (a) Toluene, 80 °C, 3 atm O_2 (Table I, Entry 15). A solution of 16.3 mg of **1** in 10 mL of reagent-grade toluene under 3 atm oxygen was heated to 80 ± 1 °C for 8 days. The solvent was removed and the product mixture analyzed by 200-MHz H NMR spectroscopy in $CDCl_3$. Except for some rather large unassigned peaks at δ 2.4 (m) and 0.8–1.5 (m), the spectrum could be attributed to unreacted **1** and a mixture of compounds **2–4**.

(b) Tetrachloroethane, ca. 150 °C, 84 atm O_2 (Table I, Entry 16). A solution of 20 mg of **1** in 5 mL of tetrachloroethane was put under 84 atm of oxygen pressure in a steel autoclave and was heated to ca. 150 °C for 2 h. This treatment gave a very complex reaction mixture containing at best a trace of any of the compounds **1-4** (TLC; 90-MHz H NMR). Similar pyrolysis under 90 atm nitrogen resulted in a clean conversion to the hydrocarbons **2** and **3**; the latter products were stable to the pyrolysis conditions under 50 atm oxygen.

Actinometry. Monochromatic light for irradiation was obtained by isolating the desired lines from a Hanau St. 41 stabilized medium-pressure mercury arc with the appropriate band-pass glass filters. The light flux entering the sample cells was determined by actinometry with azobenzene in methanol solution as described by Gauglitz and Hubig.[22] It should be noted that in eq 14–16,[22a] used for the computer-aided analysis of the spectrophotometric data, the photokinetic factor should be defined as $F = E'/(1 - 10^{-E'})$, the inverse of the definition of F given in eq 1.[22a] For actinometry at 405 nm the azobenzene solutions were preirradiated at 313 nm in order to produce larger absorbance changes upon irradiation at 405 nm. The following pseudo quantum yields $Q = \epsilon'_t\phi_{tc} + \epsilon'_c\phi_{ct}$ (ϵ'_t and ϵ'_c are the extinction coefficients of *trans*- and *cis*-azobenzene, respectively, at the wavelengths of irradiation) were used for actinometry:[22b] Q(313) nm) = 3700, Q(365 nm) = 130, Q(405 nm) = 530 M^{-1} cm^{-1}. For irradiations at 313 and 365 nm actinometry was also done with Aberchrome 540.[23] The light fluxes determined by this method were about 10% lower than those obtained with azobenzene. Since we earlier found a quantum yield slightly in excess of 1 for nitrogen elimination from the azo precursor **11** of the biradical d by using Aberchrome 540,[8] the quantum yields reported here are based on azobenzene actinometry.

Results

Spectroscopic Detection of the Triplet Biradical ^{3}b at 77 K. The azo compound **1** was dissolved in an EPA solvent mixture (1.5 × 10^{-4} M **1**, diethyl ether/isopentane/ethanol, 5:5:2) cooled to 77 K in an optical quartz dewar, and the rigid glassy solution was irradiated with monochromatic light of 405 nm. The progress of the photoreaction was monitored by recording the absorption spectra of the glass between the periods of irradiation; no spectral changes occurred during these dark intervals. Previous preparative work had shown[2b] that irradiation of **1** in a rigid glass at 77 K gave divinylnaphthalene (**3**) as the exclusive photoproduct and indeed, after exhaustive irradiation, the absorption spectrum was identical in shape and intensity with a spectrum of authentic **3** at a concentration of 1.5 × 10^{-4} M. That the clean transformation **1** → **3** was, however, not a simple photoreaction is evident from the sequence of spectra displayed in Figure 1: there are no isosbestic points, and the spectra taken in the course of the reaction exhibit additional features not present in the spectra of either **1** or **3**, namely, a weak, highly structured absorption band system in the visible (λ_{max} 512 nm) and a strong band system in the near-UV (λ_{max} 341 nm). These data were analyzed as follows.

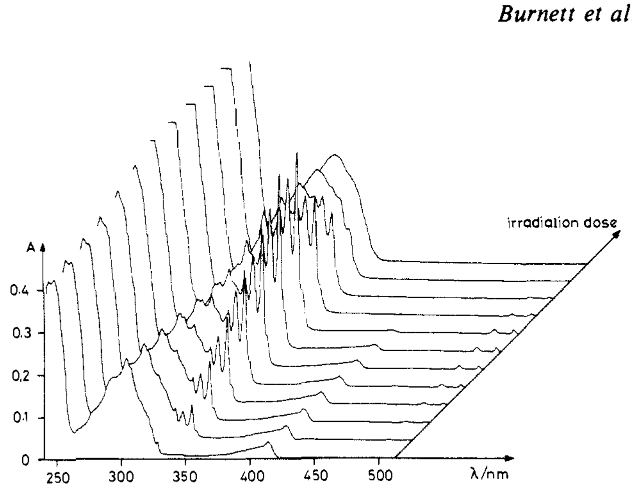

Figure 1. Spectrophotometric monitoring of the photochemical conversion of **1** to **3** in EPA glass at 77 K. Bottom curve: **1** prior to irradiation at 405 nm. Note the structured absorption bands at 340 and 512 nm due to ^{3}b in the intermediate spectra.

In a first step, the minimum number of components required by the spectral data was determined by a principal-component analysis.[24] Thus, the rank of the data matrix, **D**, which collected 1000 absorbance values for each of the 12 spectra shown in Figure 1, was found to be essentially 3, as the eigenvalues of the covariance matrix $\mathbf{DD}^t$ dropped sharply in size after the principal 3 ones and as the data matrix **D** (dimension 12 × 1000) was well reproduced, within experimental error, by $\mathbf{D} \cong \mathbf{UV}$, where **V** (3 × 1000) contains the three significant eigenvectors of $\mathbf{DD}^t$ and **U** (12 × 3) = $\mathbf{DV}^t$ contains the weighting coefficients to reproduce the 12 spectra from the 3 eigenvector spectra. This showed that one and only one component in addition to **1** and **3** was necessary to accommodate the spectral changes observed during the transformation **1** → **3**.

The second step in the analysis was to decompose the sequence of absorbance spectra into chemically meaningful quantities, namely to reconstruct the data matrix **D** from the molar absorptivities of the three components **A**(3 × 1000) and their concentration profiles through the reaction **C**(12 × 3), **D** = **CA**, according to Beer's law. A unique transformation of the abstract factors **U** and **V** to the target factors **C** and **A** can be found for ordered sets of data.[25] In the present case, the determination of the appropriate projection matrix **R** (3 × 3) to yield **A** = **RV** and $\mathbf{C} = \mathbf{UR}^{-1}$ (from **CA** = **CRV** = **UV**, hence **CR** = **U**) was straightforward, thanks to the additional information available. The first spectrum corresponded to that of the azo compound **1** and the last spectrum to that of divinylnaphthalene (**3**). Thus, the first and the last row of **R** were set equal to the first and last row of **U**, respectively. The middle row of **R** was then determined by the method of tangents described by Borgen and Kowalsky,[26] which relies on the smooth variation in the concentrations of the components along the sequence of spectra. The spectrum of the intermediate (second row of **A**, Figure 2) has been obtained previously by a less rigorous procedure.[4] The present analysis assumes a well-defined set of boundary conditions, which are justified on chemical grounds, and it makes full and unbiased use of the spectral data. As a byproduct, the matrix **C** contains essential mechanistic information, the concentration profiles of the three components (Figure 3).

In a separate experiment, the irradiation at 405 nm was interrupted when the concentration of the intermediate had reached its maximum, and the band-pass filter was replaced by a cutoff filter. By further irradiation at λ >450 nm the accumulated intermediate was converted to **3**. The resulting spectrum could

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[26] Borgen, O. S.; Kowalsky, B. R. *Anal. Chim. Acta* **1985**, *174*, 1–26, Figures 17–20.

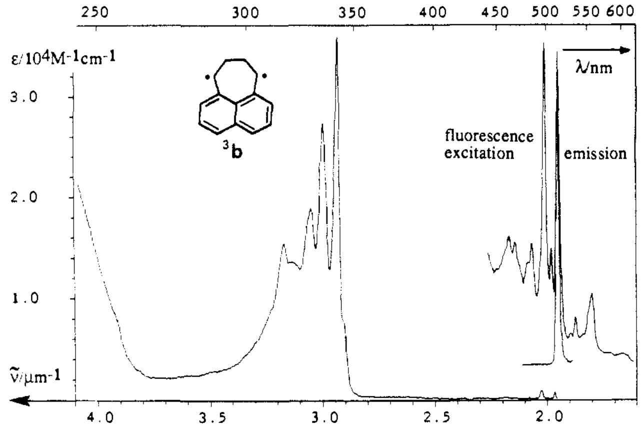

Figure 2. Absorption, fluorescence, and fluorescence excitation spectra of ^{3}b in EPA at 77 K. The absorption and excitation spectra were practically superimposable; therefore, only part of the latter is shown for clarity. The ordinate scale is based on the analysis described in the text (cf. Figure 3).

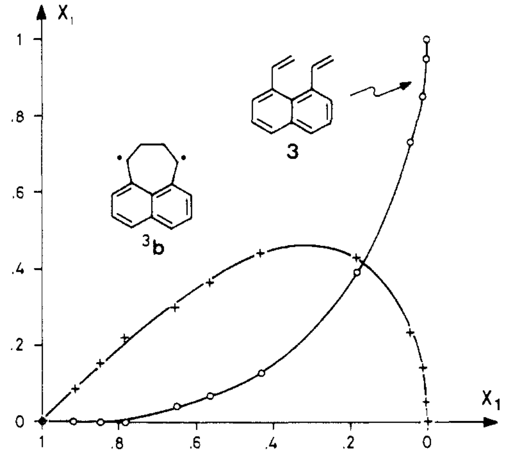

Figure 3. Concentration profiles: the mole fractions X$_i$ of ^{3}b and **3** are plotted vs the mole fraction of **1** during the photoreaction **1** → **3** in EPA at 77 K.

be analyzed as a mixture of **1** and **3** at a total concentration that was equal to the initial concentration of **1**. Thus, no optically transparent products or intermediates other than molecular nitrogen were formed. The light-sensitive intermediate (Figure 2) has been identified as the triplet biradical 1,4-perinaphthadiyl (^{3}b).[4] A semiempirical calculation for the triplet–triplet absorption spectrum of the parent chromophore ^{3}a predicted that the weak absorption band near 500 nm should contain two weak absorption bands of opposite polarization.[27] This was confirmed experimentally by the method of photoselection:[28] a sample of randomly oriented ^{3}b in poly(methyl methacrylate) glass at 77 K was partially bleached through a polarizer and a cutoff filter (λ >510 nm). The remaining sample of ^{3}b was distinctly dichroic and could be decomposed into two orthogonal spectra (Figure 4). Similar results were obtained by the irradiation of **1** with polarized light, which directly produced a dichroic sample of ^{3}b.[6]

Two other spectroscopic signals appeared when **1** was irradiated at 77 K. First, a green fluorescence emission was observed with a lifetime of 190 ± 10 ns. The intermediate absorption and emission were clearly due to the same species: the sharp 0–0 transitions of absorption and emission nearly coincided at 512 nm, and the fluorescence excitation spectrum agreed well with the absorption spectrum (Figure 2). Second, ESR spectroscopy of irradiated frozen solutions of **1** in benzene, hexafluorobenzene,

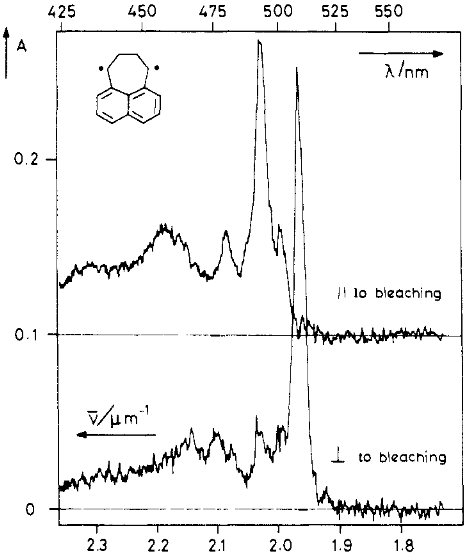

Figure 4. Resolution of the orthogonal components in the first absorption band of ^{3}b by photoselection. The upper curve (absorbance parallel to the direction of polarization of the photolyzing light I >510 nm) is shifted upward by 0.1 absorbance unit.

poly(methyl methacrylate) glass, EPA, or ethanol at 77 K gave a weak signal at half-field and a broad spectrum centered near $g = 2$; the pattern was characteristic of randomly oriented molecules in the triplet state (zero-field splitting parameters $|D/hc| = 0.018$ cm^{-1} and $|E/hc| < 0.003$ cm^{-1}). All three signals of the intermediate (absorption, emission, ESR) were wiped out by further irradiation at λ >450 nm or when the sample was thawed.

Naphthocyclobutane (**2**) was practically stable to irradiation with conventional light sources at 77 K. It exhibited strong fluorescence and phosphorescence emissions typical of an alkyl-substituted naphthalene. However, when **2** was photolyzed at 77 K with a few high-intensity flashes from an excimer laser (248 nm, ca. 100 mJ/flash, flash width at half-height ca. 20 ns), ^{3}b was readily detected and unambiguously identified by its characteristic, long-lived and structured fluorescence emission at wavelengths $\lambda \geq 512$ nm.

Quantum Yield Determinations. Quantum yields $\phi(-N_2)$ for the photoelimination of nitrogen from the azo compound **1** at ambient temperature were determined spectrophotometrically by monitoring the disappearance of the nπ^* absorption band of **1** at λ_{max} 410 nm, where none of the photoproducts had any absorption. Initial concentrations of **1** were ca. 10^{-3} M. Azobenzene was used as an actinometer (cf. the Experimental Section).[22] The direct irradiation of a hexane solution of **1** at 405 nm gave values within the range of $\phi(-N_2) = 0.56 \pm 0.02$ (six determinations). Outgassing the solutions had no effect on the quantum yield of disappearance of **1**, but it did change the product distribution (see below); the addition of 0.2 M dimethylmercury or piperylene (up to neat) did not affect either. A single determination of the quantum yield for irradiation of **1** at 313 nm, i.e., in the region of the naphthalene $\pi\pi^*$ absorption band, gave a value of $\phi(-N_2) = 0.6$.

In order to determine the quantum yield $\phi(-N_2)$ upon triplet sensitization of **1**, a solution of 1×10^{-3} M **1** with 2×10^{-2} M benzophenone in degassed acetonitrile was irradiated at 365 nm. Over 95% of the light was absorbed by the sensitizer, and control experiments by laser flash photolysis (excitation at 353 nm) showed that the triplet energy transfer from benzophenone to **1** was >99% efficient at low conversions, since the benzophenone triplet (λ_{max} 530 nm) was quenched by **1** with a rate of ca. 8×10^9 M^{-1} s^{-1}. Under these conditions, quantum yields in the range of $\phi(-N_2) = 0.32 \pm 0.02$ were determined, again by monitoring the disappearance of **1** spectrophotometrically. Considering the possible systematic errors involved in actinometry at different wavelengths, we conclude that the photochemical quantum yields for direct irradiation in the nπ^* (405-nm) and $\pi\pi^*$ (313-nm) absorption

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Table I

no.	reactant	solvent[a]	condn,[b] T/°C	O_2, P/atm	product yields/% 2	3	4	6	ϕ_2/ϕ_3	ϕ_{Ox}/ϕ_{HC}
1	**1**	Ph	$h\nu$, 20	0	84	16			5.3	0
2	**1**	Ph	$h\nu$, 20	1	57	17	26	0	3.4	0.35
3	**1**	Ph	$h\nu$, 20	4.6	36.5	6.5	57	0	5.7	1.25
4	**1**-d_2	Ph	$h\nu$, 20	1	52[c]	24[c]	24[c]	0	2.2	0.31
5	**1**	Me-cC_6H_{11}	$h\nu$, 20	1	41	12	47	0	3.4	0.91
6	**1**	Me-cC_6H_{11}	$h\nu$, −78	1	0	0	0	yes		∞
7[e]	**1**	MeOH	$h\nu$, 20	0	87	13			6.7	0
8[e]	**1**	MeOH	$h\nu$, −78	0	>98[d]	<2[d]			>49	0
9[e]	**1**	EtOH	$h\nu$, −198	0	0	100			0	0
10	**1**	MeOH	$h\nu$, 20	1	36	6	34	24	6.0	1.43
11	**1**	MeOH	$h\nu'$, −78	1	0	0	0	>50		∞
12	**1**	1-ClNp	Δ, 160	0	90	10			9.0	0
13	**1**	1-ClNp	Δ, 140	0.2	83	17	0	0	4.9	0
14	**1**	1-ClNp	Δ, 160	1	88	12	0	0	7.3	0
15	**1**	MePh	Δ, 80	3	53[d]	6[d]	41[d,f]	0	8.8	0.71
16	**1**	C_2Cl_4	Δ, ~150	84	0	0	g	g		∞[g]

[a] Ph = benzene, Me-cC_6H_{11} = methylcyclohexane, MeOH = methanol, 1-ClNp = 1-chloronaphthalene, MePh = toluene. [b] $h\nu$ = irradiation by a medium-pressure mercury arc through a UV cutoff filter (λ >380 nm), $h\nu$ = irradiation through pyrex (λ >340 nm), Δ = pyrolysis. [c] Yields refer to dideuterio derivatives of **2**–**4** (Scheme I). [d] The quoted percent yields are relative due to the formation of other products. [e] Taken from ref 2b. [f] The peroxide **4** was identified solely by H NMR, in particular by its characteristic peak at δ 5.4, as an authentic sample of **4** was not available at the time of the experiment. [g] Compounds **4** and **6** are unstable under these conditions.

bands of **1** are identical within experimental error but that the value obtained for the sensitization of **1** is significantly lower.

Flash Photolysis. The biradical ^{3}b was formed within 50 ns of the excitation flash and was easily identified by its characteristic absorption bands at 340 nm (strong) and 512 nm (weak). The rate law for the decay of the transient ^{3}b was complex, consisting of both a second-order and a first-order component. When high concentrations of the transient were produced by intense light flashes, the decay was initially dominated by the second-order component. This was unavoidable when the very weak first absorption band of ^{3}b was monitored in the visible region, because high concentrations were needed in order to obtain reasonably strong signals. Apart from this technical limitation, the decay kinetics at 340 and at 512 nm were the same, in further support of the previous claim that both of these bands were due to the same chemical species. In some experiments, up to 0.1 M piperylene was added to the solution in order to make sure that long-lived triplets such as, e.g., ^{3}**2** or ^{3}**3** did not contribute to the transient absorption. This had no effect on the decay kinetics. The decay approached first-order kinetics when the concentration of ^{3}b was low, i.e., with flashes of low intensity or toward the end of the decay, and the decay rate $^3k_{ISC}$ was then found to be close to 5×10^3 s^{-1} in degassed solvents of widely different polarity (hexane, benzene, acetonitrile, methanol). The second-order component was suppressed in highly viscous solvents; the lifetime of ^{3}b was 260 μs in poly(methyl methacrylate) glass and 180 μs in glycerol at ambient temperature. Therefore, glycerol was used to determine the temperature dependence of the first-order decay rate (Table II).

Second-order analyses of the initial parts of the decay curve gave $k/\epsilon d \cong 1 \times 10^6$ s^{-1}. The extinction coefficient ϵ(512 nm) of ^{3}b is close to 1000 M^{-1} cm^{-1} at 77 K; we have reduced this value to 500 M^{-1} cm^{-1} in order to account for the loss in fine structure at ambient temperature. This gave a value of approximately 5×10^9 M^{-1} s^{-1} for the absolute second-order decay rate of ^{3}b; a value close to the diffusion-controlled limit was expected from the fact that this reaction could be effectively suppressed in viscous solvents.

The observation of a fast second-order annihilation of ^{3}b suggested that at sufficiently high concentration a dimerization of the biradicals ^{3}b was able to compete with the monomolecular decay to **2** and **3**. A sample of 300 mg of **1** was therefore photolyzed by 120 flashes from the conventional discharge lamps. Chromatographic separation of the products showed that, in addition to the usual hydrocarbons **2** and **3** (200 mg), a new fraction (15 mg) was indeed formed that contained several dimers of b. Two new products, which amounted to ca. 70% of the dimer fraction, could be isolated and were identified by high resolution H NMR spectroscopy as one single diastereomer each of the dimers **9** and **10**. It is noteworthy that the known [4 + 4] dimer **5**[19] was not present in the reaction mixture.

Table II. Constants for the Reactions of ^{1}b and ^{3}b at Room Temperature (cf. Scheme II) and Arrhenius Parameters

reaction	symbol	rate[a]	log (A/s^{-1})	E_a/ kcal mol^{-1}
^{1}b → ^{3}b	$^1k_{ISC}$	≈1 × 10^8 s^{-1}	≈7	≤2
^{3}b → ^{1}b	$^3k_{ISC}$	5 × 10^3 s^{-1}	6.9	4.5
^{1}b + $^3O_2$ → ^{3}b + $^3O_2$	$^1k_{Ox}$	2.5 × 10^{10} M^{-1} s^{-1}		
^{3}b + $^3O_2$ → **4** or **6**	$^3k_{Ox}$	2.4 × 10^9 M^{-1} s^{-1}		
^{3}b + ^{3}b → **9** or **10**	$^3k_{Dim}$	≈5 × 10^9 M^{-1} s^{-1}		
^{1}b → **2**	$^1k_2$	≈1 × 10^9 s^{-1}	13[a]	≈5
^{1}b → **3**	$^1k_3$	≈2 × 10^8 s^{-1}	13[a]	≈7

[a] The rate constant $^1k_{ox}$ is assumed, and the values for $^1k_{ISC}$, $^1k_2$, and $^1k_3$ depend on this assumption; see text for explanations.

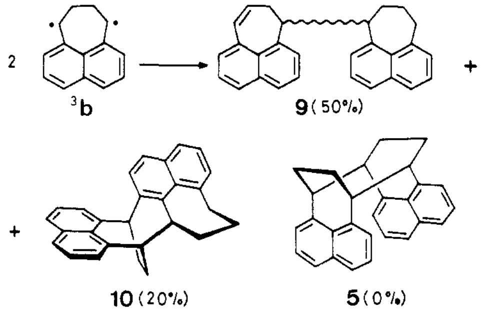


Figure 5 shows the difference in absorbance before and 12 μs after photolysis by a conventional discharge flash lamp of a degassed 3×10^{-5} M solution of **1** in hexane containing 1×10^{-3} M piperylene. In addition to the characteristic sharp absorption band of ^{3}b at 340 nm we note the negative peak around 410 nm, which arises from the depleted absorbance of **1** in that region. An important conclusion may be drawn from this difference spectrum. It is apparent that the intensity of the transient absorbance by ^{3}b at 340 nm is comparable to that of the bleaching at 410 nm. Since the extinction coefficient of ^{3}b at 340 nm is much larger than that of **1** at 410 nm, it follows that the amount of triplet biradical ^{3}b detected in solution corresponds to only a small fraction of the azo compound **1** depleted by photolysis. The spectrum was taken with a sufficiently small delay after the photolysis flash such that only a small fraction (≤25%) of ^{3}b could escape detection. As noted above, the extinction coefficient is probably lower at room temperature than the value of ϵ(^{3}b, 340

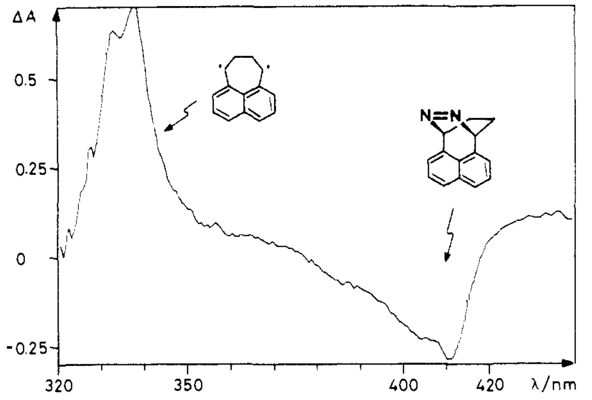
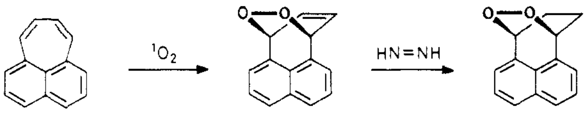


Figure 5. Spectrographic flash photolysis of **1** in degassed methanol. The ΔA spectrum displays the difference in absorbance before and 12 μs after the peak of the flash.

nm) = 36 000 M^{-1} cm^{-1} determined at 77 K due to the usual blurring of the vibrational fine structure. If we use a reduced extinction coefficient of 20 000 M^{-1} cm^{-1} and allow for a 25% loss of ^{3}b at the time the spectrum was taken, we still calculate that the yield of ^{3}b relative to the amount of **1** depleted is only 10%. This determination shows in a very direct way that the major path for nitrogen elimination from **1** upon direct irradiation at room temperature does not proceed via the intermediate ^{3}b, which is formed in a yield on the order of (but less than) 10%. Accordingly, the intensity of the transient absorption of ^{3}b did not decrease when benzophenone was added as a sensitizer, despite the lower quantum yield for sensitized nitrogen elimination.

The lifetime of ^{3}b was reduced by 3 orders of magnitude to 200 ns in air-saturated solution. A plot of the observed first-order decay rate against the partial pressure of oxygen in equilibrium with a methanol solution of **1** was linear (5 points); assuming Henry's law and using a value of $\alpha = 1.02 \times 10^{-2}$ mol dm^{-3} atm^{-1} for the solubility of oxygen in methanol at 20 °C,[29] the second-order rate constant for the quenching of ^{3}b by triplet oxygen was determined from the slope of the linear regression line as $^3k_{Ox} = (2.4 \pm 0.3) \times 10^9$ M^{-1} s^{-1}. The fivefold higher value for $^3k_{Ox}$ reported previously had been determined by an inadequate technique.[4]

Oxygen Trapping Experiments. (a) Photolyses. Since over 99% of the triplet biradicals ^{3}b were quenched by triplet oxygen in aerated solution, it was important to know what the chemical consequences of this quenching were. Preliminary experiments, in which 60-MHz H NMR spectroscopy had been used to analyze the product mixtures, suggested that the effect of oxygen was to change the relative yield of the hydrocarbon products **2** and **3**.[30] Subsequent scrutiny showed that in fact a new compound had been formed in addition to **2** and **3**. The new oxidation product could be separated from the hydrocarbons by thin-layer chromatography, but this was not feasible by column chromatography. The available spectroscopic data suggested that the new product was the cyclic peroxide **4**, and this compound was therefore synthesized by an independent procedure.



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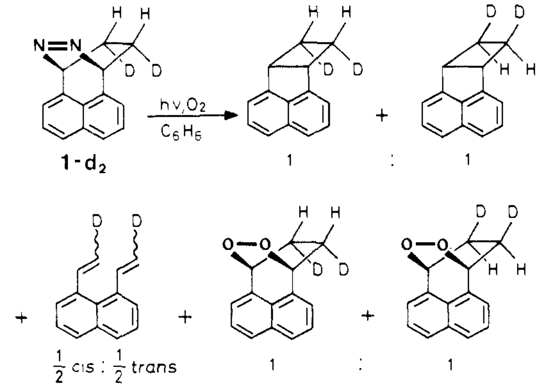
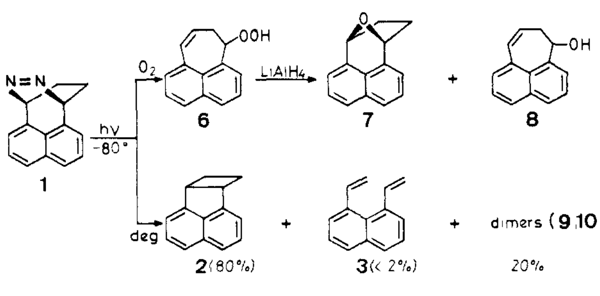


It was then easy to confirm that photolysis of **1** in benzene at room temperature under an oxygen atmosphere indeed produced the same compound **4**. Furthermore, it was obvious why **4** had not been detected in the 60-MHz spectrum of the product mixture; the resonances arising from **4** were buried by those of **2** and **3**. However, at 200 MHz and above, the bridgehead and methylene signals due to **2** and **4** and the terminal vinyl hydrogens of **3** were all resolved. Integration of these peaks in the product mixture showed that it contained 26% of the cyclic peroxide **4** in addition to the two hydrocarbons **2** and **3** (74%), which were formed in a ratio similar to that found in the absence of oxygen. No resonances due to compounds other than **2**–**4** were present in the H NMR spectrum, and control experiments showed that **2**–**4** were stable to the irradiation conditions used for their formation. Further oxygen trapping experiments, which were performed with different solvents, different oxygen pressures, and lower temperatures, were analyzed similarly as described in the Experimental Section. The results, together with some pertinent results of previous work,[2b] are collected in Table I. A number of points need explicit comments.

Previous work with the deuteriated azo compound **1**-d_2 has shown that its thermal and photochemical decomposition proceeds through a planar or effectively (by conformational equilibration) planar intermediate.[2b] It was now of interest to know the effect of oxygen on the stereochemistry of the reaction. Photolysis of **1**-d_2 in benzene under an oxygen atmosphere at room temperature gave a product distribution similar to that observed with **1**, except that the amount of divinylnaphthalene (**3**-d_2) was abnormally high (24%). Owing to the small amount of deuteriated sample available, we have not attempted to establish whether this difference is real and does represent an isotope effect on the product distribution. The analysis of the products' NMR spectra after chromatographic separation did, however, leave no doubt that the deuterium label was randomized not only in the hydrocarbon products **2**-d_2 and **3**-d_2 but also in the peroxide **4**-d_2, i.e., half cis and half trans in 1,8-divinylnaphthalene and half exo-cis and half endo-cis in the other two products (Scheme I). One must conclude that an effectively planar transient is involved in the formation of all three products.

In methanol solution, yet another oxidation product, the hydroperoxide **6**, was formed in the presence of oxygen. This was found to be the major product (up to 70%) when an oxygenated solution of the azo compound **1** in methanol was irradiated (λ >340 nm) at dry ice/acetone temperature. No hydrocarbons (**2**, **3**) or cyclic peroxide (**4**) were formed under these conditions, and we believe that the unidentifiable 30% side products were formed by secondary photolysis of the new compound. These results should be contrasted to those obtained in the absence of oxygen where the isomeric hydrocarbons **2** and **3** and the dimers **9** and **10** were formed.



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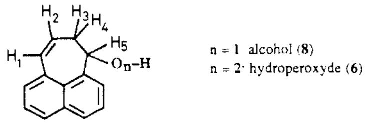
(29) Schäfer, K.; Lax, E. In *Landolt-Börnstein*, 6th ed.; Springer-Verlag: Berlin, 1962; Vol. II, Part 2. Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1–9. Battino, R.; Rettich, T. R.; Tominaga, T. *J. Phys. Chem. Ref. Data* **1983**, *12*, 163–178.

(30) Footnote 12 of ref 4.

Table III. Comparison of H NMR Spectra of **6** and **8** in $CDCl_3$



	hydroperoxide **6**		alcohol **8**	
assignment	chem shift, δ/ppm	multiplicity,[a] J/Hz	chem shift, δ/ppm	multiplicity,[a] J/Hz
aromatic	7.1–7.9	m	7.1–7.7	m
H_1	6.75	dd (11.8, 2.4)	6.6	d (12)
H_2	5.91	dt (11.8, 3–4)	5.8	dt (12, 5)
H_3, H_4	3.00	m	2.7	m
H_5	5.40	m	5.0	m
OH	not assigned		3.0	br s

[a] m = multiplet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, br s = broad singlet.

The hydroperoxide **6** could not be isolated due to its instability on silica gel but was identified on the basis of spectroscopic data obtained with the crude product mixture and of chemical evidence as follows. The infrared spectrum of the photolysis mixture in CH_2Cl_2 showed an OH stretching band at 3500 cm^{-1}, a value typical for hydroperoxides.[31] The H NMR spectrum of the major component, whose resonances were easily distinguished from the much smaller resonances associated with impurities, was similar to the spectrum of the corresponding alcohol **8** (Table III).[20,21] As the compound did not survive column chromatography, the reaction mixture was reduced with $LiAlH_4$; this gave the cyclic ether **7** and the alcohol **8** as the major products. The mass spectra and H NMR spectra of these products were identical with those of authentic samples.[20,21] The cyclic ether **7** most likely arose by acid-catalyzed cyclization of the alcohol **8** during the hydrolysis of the lithium salts formed in the reaction.

The hydroperoxide **6** was stable in methanol and deuteriochloroform at room temperature for extended periods of time but decomposed completely in benzene within less than 12 h. Thus, had the hydroperoxide been formed in the photodecomposition of the azo compound **1** in benzene under oxygen at room temperature, it would probably not have been detected. The formation of **6** in benzene is, however, unlikely because all the resonances in the 200-MHz H NMR of the product mixture could be assigned to the known compounds **2**–**4**. Control experiments have shown that both **4** and **6** are sensitive to short-wavelength irradiation but that **4** is not converted to **6** or vice versa.

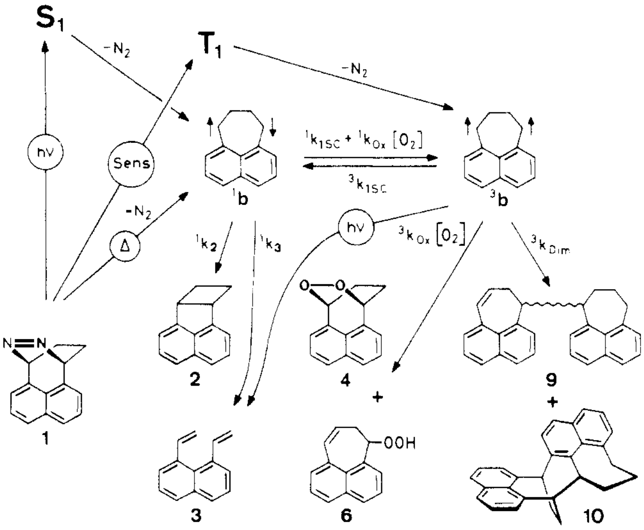
(b) Thermolyses in the Presence of Oxygen. Pyrolysis of the azo compound **1** in 1-chloronaphthalene in the presence of air at 140 °C and in oxygen-saturated 1-chloronaphthalene at 160 °C did not yield any oxygenated products; the two hydrocarbons **2** and **3** were formed in a ratio similar to that found upon thermolysis at 160 °C in the absence of oxygen (Table I, entries 12–14).

Heating a solution of **1** in toluene to 80 °C under 3 atm of oxygen pressure for 8 days yielded a complex product mixture that in addition to unreacted **1** and the hydrocarbons **2** and **3**, contained an equal amount of the cyclic peroxide **4** (Table I, entry 15). The hydrocarbons **2** and **3** could not be detected in the product mixture formed by pyrolysis of **1** at ca. 150 °C under 84 atm of oxygen pressure, although both **2** and **3** could largely be recovered after exposure to such conditions. Thin-layer chromatograms indicated an extremely complex product mixture but were empty at low retentions where **2** and **3** would have appeared.

Discussion

The goal of this work was to gain information about the reactivity of the singlet and triplet state of the biradical 1,4-perinaphthadiyl (b) and to study how its reactions depend on the solvent, the temperature, and the presence of trapping reagents.

Scheme II



Scheme II shows the most economical reaction mechanism, which can account for all the results and shall be defended below. The product yields obtained under various reaction conditions are collected in Table I and the rate constants determined or estimated for the reactions of singlet and triplet b at room temperature are given in Table II.

Photoreactions at Low Temperature. 1,4-Perinaphthadiyl was first detected by its characteristic ESR spectrum, which was observed after the photolysis of **1** in rigid glassy solvents at low temperature.[2b] Originally, the ESR signal intensities of samples of b, as well as those of the related biradicals a[2a] and c,[3] were found not to be proportional to $1/T$, the temperature dependence expected for molecules with a triplet ground state (Curie's law). These findings were attributed to a temperature-dependent change in the Boltzmann population of the singlet and triplet state, and it was concluded that these biradicals have a singlet ground state.[2,3] However, an effort to detect corresponding changes in the absorption spectrum of b as a function of temperature has failed, and subsequent reinvestigations of the ESR spectra showed that the deviations observed previously must have been artifacts; provided that microwave powers below 10 μW were used, significant deviations from Curie's law were not observed down to ca. 10 K.[4,5a,9a] Strictly speaking, all of these observations still do not prove that the triplet state is the ground state of b; they are also consistent with the singlet- and triplet-state energies being equal to within a few tens of calories per mole. Such a close accidental degeneracy would, however, be quite fortuitous for any single compound in one solvent. Since the singlet state should be much more susceptible to substituent and solvent effects than the triplet state,[1d] it is highly improbable that such a degeneracy would occur for several derivatives and in various solvents of widely different polarity. Platz has reported Curie law behavior even for heteroatom-substituted derivatives of a.[5b,5d] *We conclude that the triplet state is the ground state of b.*

The exhaustive irradiation of **1** in a rigid glassy solution at 77 K yields a single product, divinylnaphthalene (**3**). This reaction proceeds in two photochemical steps, as can be seen from the concentration profiles obtained by spectrophotometric analysis (Figure 3): The product of the first photoreaction is the triplet biradical ^{3}b, which is stable in the dark at 77 K. The final product **3** is formed only after an "induction period", when the biradical intermediate ^{3}b begins to accumulate. This explains the striking trend reversal found in the relative yield of products **2** and **3** as the reaction temperature is lowered. In fluid solution ^{3}b decays thermally and yields predominantly **2**, and the selectivity increases as the temperature is lowered. At 77 K, however, ^{3}b reacts photochemically giving **3**. Thus, the product ratio of **2** to **3** increases from ca. 5 at 20 °C to >50 at -78 °C and then suddenly drops to zero at 77 K (Table I). The preparative work then provides independent and more quantitative evidence for the qualitative spectroscopic observation that *^{3}b is the only product*

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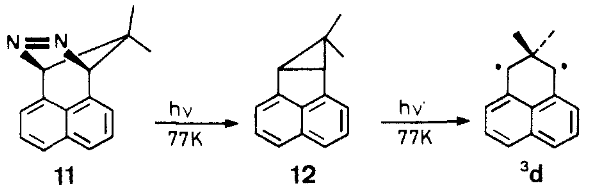
(31) Nakanishi, K. *Infrared Absorption Spectroscopy*; Holden-Day: San Francisco, 1962. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 2nd ed.; Chapman & Hall: London, 1980; Vol. 2.

*formed by the irradiation of **1** at 77 K and that the final product **3** is formed only by secondary photolysis of ^3b.* The question, at which point intersystem-crossing to the triplet manifold takes place, will be discussed below. At this point we note only that entirely different results were recently obtained with the related azo compound **11**:[8] The irradiation of **11** at 77 K gave the naphthocyclopropane **12** directly, and the triplet biradical 1,3-perinaphthadiyl (^{3}d) was not formed (<0.5%) from **11**, but only by secondary photolysis of **12**. The pathway for the formation of ^{3}d from **12** at 77 K has been determined as $S_1(\mathbf{12}) \rightarrow T_1(\mathbf{12}) \rightarrow {}^3$d.



Reactions in Degassed Solution. The quantum yield of nitrogen elimination amounts to ca. 0.6 upon direct irradiation of **1** and to 0.3 upon sensitization with benzophenone. The value for direct irradiation is not affected by external heavy atoms, by the addition of piperylene, or by the wavelength of irradiation (405 or 313 nm). Recall that the photolysis of the azo precursor to parent 1,8-naphthoquinodimethane (a) is wavelength dependent; nitrogen elimination is initiated only by $\pi\pi^*$ excitation of the naphthalene chromophore, whereas $n\pi^*$ excitation of the azo group gives rise to cis–trans isomerization of the N=N double bond.[2a,32] We have not been able to detect any fluorescence emission of **1** on a conventional fluorescence spectrometer nor even by laser flash excitation at 77 K ($\phi_f < 10^{-5}$); thus the lifetime of $S_1(\mathbf{1})$ must be very short ($\tau_f = \phi_f k_f < 2$ ps, where $k_f \cong 5 \times 10^6$ s^{-1} was estimated from the intensity of the $n\pi^*$ absorption band). Since the quantum yield for nitrogen elimination is twice as high for direct irradiation than for sensitization, we can state that *upon direct irradiation at room temperature most, if not all, of the nitrogen elimination takes place very rapidly in the excited singlet state of **1**.* Nevertheless, the quantum yield for nitrogen elimination is significantly less than unity in both the singlet and the triplet excited states of **1**. The reversible formation of a diazenyl biradical (one C–N bond of **1** broken)[33] or an incipient inversion of a nitrogen atom[34] may be considered as processes responsible for the deactivation of the excited state without chemical consequences. If a diazenyl biradical occurs as an intermediate, it does not directly precede the formation of the end products. The complete scrambling of the deuterium labels in all the products formed from the azo compound **1**-d_2 (Scheme I) shows that some nitrogen-free, effectively planar intermediate must be involved.

The triplet biradical (^{3}b) is readily detected as a reactive intermediate by flash photolysis of **1**, but in contrast to the results at 77 K mentioned above, a spectrographic comparison of the generated transient absorbance with the depleted absorbance of the starting material (Figure 5) shows that *at room temperature ^3b is formed only as a minor side product in about 10% relative yield upon direct excitation of **1**.* The fact that ^{3}b is the sole product formed by excitation of **1** at 77 K suggests that at some intermediate stage of the reaction there is a competition between a thermally activated chemical reaction and temperature-insensitive ISC. The first candidate for such behavior is the lowest excited singlet state $S_1(\mathbf{1})$, and in fact, some precedent cases in azoalkane photochemistry are well documented.[35] A second candidate is the singlet biradical (^{1}b). If there were appreciable barriers to N_2 loss from $S_1(\mathbf{1})$, one would expect **1** to be fluorescent, at least at low temperature; we have not been able to detect any fluorescence of **1** at 77 K using a quite sensitive setup. On the other hand, we know that there must be a barrier to the decay of ^{1}b, since the deuterium labels in the decomposition products of **1**-d_2 are completely scrambled under conditions where most of the reaction does not proceed via ^{3}b, i.e., upon direct photolysis or pyrolysis. Since the intermediate ^{1}b is also required by the oxygen trapping data discussed in the next section, we drop $S_1(\mathbf{1})$ on the basis of Occam's razor and identify ^{1}b as the branching point for temperature-dependent ISC.

The decay of ^{3}b to yield the hydrocarbons **2** and **3** again involves a multiplicity change. We have pointed out some time ago that the spin-forbidden nature of the rate-determining step was born out by the sensitivity of the decay rate to heavy atoms in the solvent and by the unusually low value of the preexponential factor log $(A/\mathrm{s}^{-1}) = 6.9$ determined from the temperature dependence of the decay rate.[4] The fact that the ratio of the hydrocarbon products **2** and **3** depends only on temperature but not on the previous history (photolysis, sensitization, pyrolysis of **1**) supports the assumption that the decay of ^{3}b proceeds via thermally equilibrated ^{1}b. *The observed monomolecular decay rate of ^3b at room temperature is therefore associated with the rate of the reaction $^3b \rightarrow {}^1b$* ($^3k_{\mathrm{ISC}}$, Scheme II), since this reaction is essentially irreversible. Recently, Fischer and Michl reported very elegant work on the monomolecular decay of the related triplet biradical 1,3-perinaphthadiyl (^{3}c) and derivatives thereof.[9b] These authors found a temperature-independent contribution to the decay rate of ^{3}c that was attributed to tunneling. External and internal heavy-atom effects were expressed by a comparable increase of the log *A* value for the temperature-independent and the thermally activated segments in the Arrhenius plots, which was taken as conclusive evidence for the spin-forbidden nature of the reaction.

*A second-order component in the decay curves of ^3b suggested that dimerization of the biradical was competing with its monomolecular decay to the hydrocarbons **2** and **3**.* The absolute value of this second-order rate constant was $^3k_{\mathrm{Dim}} \cong 5 \times 10^9$ M^{-1} s^{-1}. Dimers of ^{3}b had previously escaped detection, since they were formed only in trace amounts by diffuse and continuous irradiation of **1**. However, the photolysis of a degassed solution of **1** by repetitive flashing gave, in addition to **2** and **3**, a mixture of dimers in ca. 10% total yield. It was realized only later that a still higher yield of dimers could have been obtained by flash photolysis of **1** at reduced temperature, since this would have given a higher yield of ^{3}b as shown above. The laborious preparative work was not repeated, but TLC separation of a small sample flash photolyzed at −78 °C and analysis of the fractions by UV indeed indicated that at least 20% dimers had been formed under these conditions.

The dimer fraction contained **9** and **10** as major components, but we have found none of the two isomeric dinaphthocyclooctanes that were expected as the "straightforward" [4 + 4] dimers of ^{3}b. Actually, the head-to-head isomer **5** was available independently by hydrogenation of the photodimer of pleiadiene,[19] and this isomer would have been detected even as a minor component of only a few percent of the dimer fraction. Molecular models suggest that the [4 + 4] dimers are quite strained, and this is supported by the "forbidden" but facile thermal rearrangement observed with the pleiadiene photodimer.[19] This may explain why ^{3}b does not form [4 + 4] dimers.

Reactions in Oxygenated Solution. Attempts to trap the biradical intermediate b were made with various reactants including SO_2, NO, acetic acid, tricarbonylcyclobutadieneiron, methyl viologen and dienophiles. The first three reagents were successful inasmuch as new products were formed in their presence at the expense of the normal hydrocarbon products naphthocyclobutane (**2**) and divinylnaphthalene (**3**), but the resulting product mixtures were complex and rather intractable and were not suited for quantitative analysis. On the other hand, all attempts to trap b by cycloaddition to dienophiles have failed. E.g., the photolysis of **1** in neat acrylonitrile resulted in some polymer formation, but no products of low molecular weight apart from **2** and **3** could

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(32) Gisin, M.; Wirz, J. *Helv. Chim. Acta* **1976**, *59*, 2273–2277.

(33) Bigot, B.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1978**, *100*, 2639–2642. LeFevre, G. N.; Crawford, R. J. *Ibid.* **1986**, *108*, 1019–1027. Adams, J. S.; Burton, K. A.; Andrews, B. K.; Weisman, R. B.; Engel, P. S. *Ibid.* **1986**, *108*, 7835–7838. Adam, W.; Dörr, M. *Ibid.* **1987**, *109*, 1240–1241.

(34) Rau, H.; Lüddecke, E. *J. Am. Chem. Soc.* **1982**, *104*, 1616–1620.

(35) Turro, N. J.; Renner, C. A.; Waddell, W. H.; Katz, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 4320–4322; Chang, M. H.; Dougherty, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 2333–2334. We are grateful to a reviewer for raising this issue.

be isolated. Therefore, only the results of oxygen trapping are reported and discussed in detail.

The triplet biradical ^{3}b is quenched very efficiently by triplet oxygen; in aerated solution at room temperature only 1 out of 1000 triplet biradicals escapes the quenching reaction. The reaction of ^{3}b with triplet oxygen to yield an oxidation product **4** or **6** in the singlet ground state is a spin-allowed process, if the overall multiplicity of the encounter complex [^{3}b + $^3O_2$] is singlet, i.e., in one out of nine encounters.[36] The observed second-order rate of oxygen quenching, $^3k_{Ox} = 2.4 \times 10^9$ M^{-1} s^{-1}, is indeed close to one-ninth the rate of diffusion for O_2 and thus agrees well with the value expected from spin statistics, assuming that both the quintet and the triplet encounter complexes of ^{3}b and $^3O_2$ are unreactive. This indicates that catalyzed ^{3}b → ^{1}b ISC is inefficient, as would be expected if the energy of ^{3}b is significantly below that of ^{1}b. The precise value found for $^3k_{Ox}$ should, however, be interpreted with caution: the oxygen quenching rate for ^{3}d is still lower, $^3k_{Ox} = 1 \times 10^9$ M^{-1} s^{-1},[8] presumably because the attack by oxygen at a neopentyl site is sterically hindered, and the quenching rate of 1,3-cycloalkadiyls with a saturated radical center is as high as $^3k_{Ox} = 2 \times 10^{10}$ M^{-1} s^{-1},[37] possibly due to the irreversible formation of peroxy biradicals from triplet encounter complexes.

Since the hydroperoxide **6** was found to be thermally unstable in apolar solvents and also somewhat sensitive to the irradiation conditions (λ >340 nm) used at -78 °C, the results of the product analyses from the reactions under oxygen (Table I) must be taken with a grain of salt. Nevertheless, two important and clear-cut trends are obvious from these data: (a) With sufficient oxygen pressure it is possible to suppress the formation of hydrocarbons entirely in both the photochemical and the thermal decomposition of **1** and over the whole temperature range investigated (+160 to -78 °C). At room temperature the yield of **4** increases from 26% at 1 atm to 57% at 4.6 atm of oxygen pressure. (b) Under 1 atm oxygen, the yield of oxidation products increases with decreasing temperature from virtually nil at 160 °C, to 25–50% (depending on the solvent) at room temperature, and to near 100% at −78 °C. These results cannot be attributed simply to the trapping of ^{3}b by oxygen. If this were the only way oxygen interfered in the reaction, then we would expect at most a 10% yield of peroxide, since the yield of ^{3}b is only 10%. Furthermore, from the direct observation of ^{3}b by flash photolysis, we know that oxygen quenching is by far the dominant decay process (99.9%) of ^{3}b in air-saturated solution. Therefore, this process will not contribute to a higher trapping efficiency when the oxygen pressure is further increased.

The observed increase in the yield of peroxides at elevated oxygen pressure requires that oxygen interacts with some further intermediate other than ^{3}b. We have shown above that nitrogen elimination from the excited singlet state of **1** occurs on a subpicosecond time scale, too fast to allow for diffusional encounters of S_1(**1**) with oxygen under ordinary pressures, and in any case, S_1(**1**) cannot be involved in pyrolysis. On the other hand, there is evidence that the singlet biradical ^{1}b is a true intermediate. An encounter between ^{1}b and triplet oxygen could lead to the formation of peroxides either directly or by inducing ISC of ^{1}b to ^{3}b, followed by diffusional trapping of ^{3}b by another molecule of oxygen, as shown in Scheme II. Application of the steady-state approximation to the kinetic Scheme II gives the following expression for the ratio of the quantum yields of peroxide formation (**4** and **6**) to hydrocarbon formation (**2** and **3**) as a function of oxygen concentration:

$$\frac{\phi_{Ox}}{\phi_{HC}} = \frac{{}^3k_{Ox}[O_2]({}^1k_{ISC} + {}^1k_{Ox}[O_2])}{({}^1k_2 + {}^1k_3)({}^3k_{ISC} + {}^3k_{Ox}[O_2])}$$

In air-saturated solution and at higher oxygen pressures the lifetime of ^{3}b is dominated by oxygen quenching, ${}^3k_{ISC} \ll {}^3k_{Ox}[O_2]$. The above expression then simplifies to

$$\frac{\phi_{Ox}}{\phi_{HC}} \cong \frac{{}^1k_{ISC}}{{}^1k_2 + {}^1k_3} + \left(\frac{{}^1k_{Ox}}{{}^1k_2 + {}^1k_3}\right)[O_2]$$

The product ratios ϕ_{Ox}/ϕ_{HC} found under 1 and 4.6 atm oxygen (Table I, entries 2 and 3) yield an intercept ${}^1k_{ISC}/({}^1k_2 + {}^1k_3) = 0.1$ and hence a value of ca. 9% for the quantum yield of spontaneous ISC ^{1}b → ^{3}b at room temperature, $\phi_{ISC} = {}^1k_{ISC}/({}^1k_2 + {}^1k_3 + {}^1k_{ISC})$. The excellent agreement of this value with the one determined independently by flash photolysis (vide supra) is gratifying. Alternative schemes for the oxidation of ^{1}b, either in one step or via a peroxy biradical, lead to the same approximate relationship between ϕ_{Ox}/ϕ_{HC} and oxygen pressure. However, the direct formation of a peroxide by the addition of $^3O_2$ to ^{1}b is inhibited by the spin barrier, and the formation of a peroxy biradical is likely to be rather slower than addition of oxygen to the benzyl radical, $k \cong 2.5 \times 10^9$ M^{-1} s^{-1},[38] because the radical sites in ^{1}b are secondary and the resonance energy changes upon peroxy radical formation should be comparable for benzyl and ^{1}b (the structure count ratio[39] happens to be equal to 2.5 for both reactions). On the other hand, there is no reason to doubt that the rate of oxygen-catalyzed ISC is limited only by the rate of diffusion, since the reaction ^{1}b + $^3O_2$ → ^{3}[^{3}b···$^3O_2$] → ^{3}b + $^3O_2$ is a spin-allowed, moderately exothermic process. There is ample precedence from fluorescence-quenching measurements that the rates of oxygen-catalyzed ISC are in the range of (2–3) × 10^{10} M^{-1} s^{-1}.[40] If we then *assume* that the reaction of ^{1}b with $^3O_2$ occurs with a rate of ${}^1k_{Ox} \cong 2.5 \times 10^{10}$ M^{-1} s^{-1}, the remaining unknown rate constants can be calculated from the observed ratios of ϕ_{Ox}/ϕ_{HC} and ϕ_2/ϕ_3 (Table I, entries 2 and 3). We use $\alpha = 9.1 \times 10^{-3}$ mol dm^{-3} atm^{-1} for the solubility of oxygen in benzene at 20 °C[29] and thus obtain the rate constants given in Table II. The lifetime of the singlet biradical ^{1}b is estimated as $\tau(^1\text{b}) = 1/({}^1k_2 + {}^1k_3 + {}^1k_{ISC}) \cong 1$ ns. This may be considered as a lower limit inasmuch as the assumed value for ${}^1k_{Ox}$ represents the upper limit of diffusion control. Assuming a lower value for ${}^1k_{Ox}$ would have led to proportionally lower values for ${}^1k_2$, ${}^1k_3$, and ${}^1k_{ISC}$ and thus to a higher value for $\tau(^1\text{b})$.

The rates ${}^1k_2$ and ${}^1k_3$ correspond to spin-allowed, monomolecular rearrangement processes. We may assume that their temperature dependence is well described by an Arrhenius expression with a standard preexponential factor A of ca. 10^{13} s^{-1}. The lifetime of 1 ns estimated above for the singlet biradical at room temperature then requires barriers E_a of ca. 5 and 7 kcal mol^{-1} for the processes ^{1}b → **2** and ^{1}b → **3**, respectively. On the basis of these Arrhenius expressions we are in a position to *predict the predominant decay paths of ^{1}b at temperatures above and below ambient*; it turns out that these predictions fit quite well with experimental observations. The lifetime of ^{1}b at 150 °C (conditions for the pyrolysis of **1**) is estimated as ca. 100 ps, and at −78 °C we obtain 10 ns. Since the changes with temperature in the rate of diffusion and in the concentration of oxygen at constant pressure should roughly compensate each other, one would expect very little oxygen trapping for pyrolysis under ≤1 atm oxygen, as is observed (Table I, entries 13 and 14). However, oxygen trapping should be quite efficient under 84 atm oxygen at 150 °C as well as under 1 atm at −78 °C, and this is indeed found (Table I, entries 6, 11, and 16). The ratio of **2** to **3** should increase as ${}^1k_2/{}^1k_3$ with decreasing temperature; for −78 °C we calculate ${}^1k_2/{}^1k_3 \cong 200$, in agreement with the experimental value (>49). Finally, for the quantum yield of ISC from ^{1}b to ^{3}b at 77 K, $\phi_{ISC} = {}^1k_{ISC}/({}^1k_2 + {}^1k_3 + {}^1k_{ISC})$, we obtain unity in agreement with observation.

While it is reassuring that the single hypothesis of a metastable singlet biradical ^{1}b is thus able to accommodate a large body of

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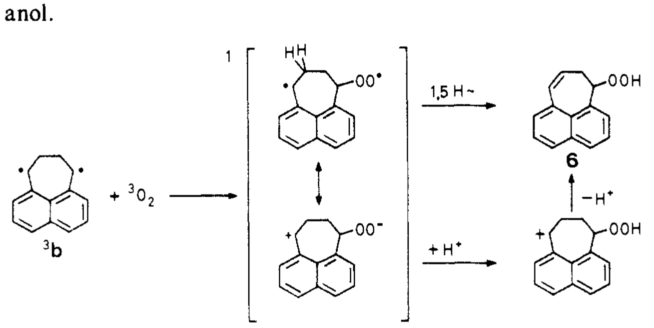
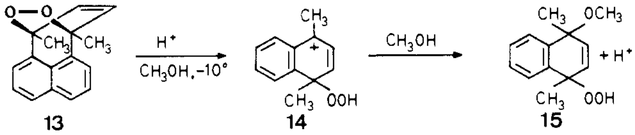
observations, we fully agree with the following statements of a reviewer: "...mechanistic interpretation of the results includes some surprising conclusions. The most remarkable is the extremely long lifetime of ^{1}b. I think most investigators would expect a singlet biradical of this type to have a lifetime on the order of picoseconds, not nanoseconds. It is not at all apparent where the 5–7 kcal/mol barriers to highly exothermic, spin-allowed reactions of ^{1}b could originate". We give here a tentative explanation. The PPP SCF SCI calculations[27] used to calculate the absorption spectrum of ^{3}a predict two low-lying singlet states belonging to the A_1 and B_2 symmetry species of the C_{2v} point group, respectively. The "closed-shell" A_1 state is the lowest singlet state for planar a, but when one of the exocyclic methylene groups is slightly rotated, the state derived from the "open-shell" B_2 state is strongly stabilized; at 30° rotation the open-shell state is predicted to lie about 1 eV below the closed-shell state, which is naturally correlated with the closed-shell product acenaphthene. While we certainly do not wish to claim any quantitative accuracy for such a calculation, the qualitative result may explain the much shorter lifetime of ^{1}c and ^{1}d, which are presumably planar,[9] as compared with ^{1}b, which is probably somewhat distorted.

The preferred product of oxidation at low temperature in methanol is the hydroperoxide **6**, at ambient temperature in benzene or methylcyclohexane it is the cyclic peroxide **4** (Table I). To see if the nature of the solvent or the temperature was the decisive factor in determining the photooxidation product, the photolysis of **1** was performed in oxygenated methylcyclohexane at dry ice temperature. When first attempted, an intractable mixture of unidentified products was obtained. In a second run, the photolysis time was reduced significantly; even here there was a considerable amount of particulate matter in the solution that had not been formed in methanol. Note that the reaction was also clean when run in methylcyclohexane at room temperature, yielding a mixture of the two hydrocarbons **2** and **3** and the cyclic peroxide **4**. None of these were found by TLC and H NMR analysis after photolysis at −78 °C. Surprisingly, the H NMR revealed the presence of **6** in low yield (13%). It is not clear why this reaction was less clean than the one in methanol. The experiment does show, however, that the solvent alone is not responsible for the formation of **6** rather than **4** at low temperature. Note that in methanol at room temperature all four products **2–4** and **6** were formed and that the ratio of **2** to **3** was the same in the presence and absence of oxygen.

What is the mechanism for the formation of **6**? The preference for **6** at low temperature suggests that **6** might be formed by a concerted process analogous to the ene reaction, whose activation energy is lower than that for the formation of the strained cyclic peroxide **4**. However, there seems to be no precedent for such a reaction.[11] Stepwise reactions may be considered where the biradical first adds $^3O_2$ to yield a peroxy biradical intermediate. The hydroperoxide **6** could then be formed either by an intramolecular 1,5 H shift or by a proton-transfer reaction. The latter process would account for the preferred formation of **6** in methanol.



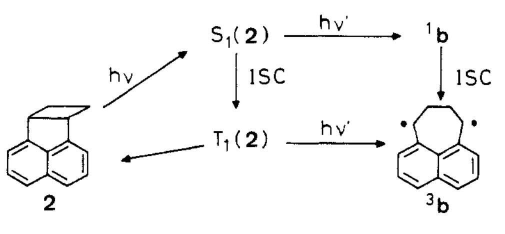
Jefford et al. prepared hydroperoxycarbocations close in structure to the one proposed in this last pathway.[41] Without exception, the hydroperoxycarbocations react with the hydroxylic solvent. In the example most relevant to the present case, treatment of the cyclic peroxide **13** with methanol/H$^+$ at −10 °C



yielded the methoxy adduct **15**, presumably by reaction of the carbocation **14** with methanol. In our case there is no evidence for the formation of a corresponding methoxy adduct. This leaves the 1,5 hydrogen shift as the most probable path to **6**.

The free energy difference $\Delta_{ST}G^{\ominus}(298\ K)$ between the singlet and triplet states of b can be estimated from the ratio of the ISC rate constants $^3k_{ISC}/^1k_{ISC}$. The efficiency of ISC from ^{1}b to ^{3}b is about 10% within the lifetime of ca. 1 ns, hence $^1k_{ISC} \cong 1 \times 10^8\ s^{-1}$. The rate of the reverse reaction ^{3}b → ^{1}b is taken to be equal to the first-order decay rate of ^{3}b, $^3k_{ISC} = 5 \times 10^3\ s^{-1}$, as mentioned above. We thus obtain $K_{ST}(298\ K) = {}^3k_{ISC}/{}^1k_{ISC} \cong 5 \times 10^{-5}$ and $\Delta_{ST}G^{\ominus}(298\ K) = -R(298)\ \ln K_{ST} \cong 6\ kcal\ mol^{-1}$. This explains why oxygen-catalyzed ISC from ^{3}b to ^{1}b is inefficient. Assuming that the electronic degeneracy of the triplet state is the dominant contribution to the entropy difference, $\Delta_{ST}S^{\ominus} \cong -R \ln 3$, the enthalpy difference is estimated as $\Delta_{ST}H^{\ominus}(298\ K) = \Delta_{ST}G^{\ominus}(298\ K) + T\Delta_{ST}S^{\ominus}(298\ K) \cong 5\ kcal\ mol^{-1}$. Comparison of this value with the Eyring parameter $\Delta H^{\ddagger} \cong 4\ kcal\ mol^{-1}$ determined from the temperature dependence of the decay rate of ^{3}b in degassed solution confirms that, within the rather large limits of error estimated at ±2 kcal mol^{-1}, singlet to triplet ISC is an activation-free process, inhibited only by the spin barrier.

Photochemical Ring Cleavage of Naphthocyclobutane (2). The photophysical properties of **2** differ strikingly from those of the related naphthocyclopropane (6b,7a-dihydro-7*H*-cycloprop[*a*]-acenaphthylene, **16**) and its dimethyl derivative **12**. With the naphthocyclopropanes **12** and **16** the fission of the peri-bridging C–C bond to yield the singlet biradicals ^{1}d or ^{1}c, respectively, is so rapid that fluorescence or ISC is completely suppressed at room temperature; at 77 K **12** does emit fluorescence and undergo ISC, but the triplet state is very short-lived due to the rapid formation of ^{3}d.[8] In contrast, the naphthocyclobutane (**2**) behaves like a normal alkyl derivative of naphthalene: it emits strong fluorescence and yields a long-lived triplet state by ISC, which is readily observed both by its triplet–triplet absorption and by phosphorescence emission at low temperature. We have not been able to detect the formation of ^{3}b by continuous photolysis of **2** at 77 K. However, Plaas and Schäfer recently reported that **2** and related cyclobutanes and cyclobutenes were efficiently photolyzed by high-intensity pulsed laser light (I > MW/cm^2).[42] This was attributed to consecutive two-photon absorption to high-lying excited states in agreement with previous related work.[43] We have confirmed this observation with **2** using an excimer laser



operating on KrF (248 nm) and have found that the triplet biradical ^{3}b is among the primary photoproducts formed by high-intensity photolysis of **2** at 77 K. We have not established whether the formation of ^{3}b proceeds via highly excited singlet or triplet states or both. The stability of **2** to conventional photolysis at

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77 K (in spite of the long triplet lifetime of **2**) tends to support the former pathway.

The marked difference between the photochemical reactivity of the naphthocyclopropanes (**12**, **16**) and naphthocyclobutane (**2**) cannot be explained on the basis of thermochemical arguments, since the strain release upon C–C bond cleavage is comparable for all three compounds. However, a simple explanation may be sought in the much bigger $\sigma\sigma^*$ excitation energy of cyclobutane compared with cyclopropane.[44] The higher propensity of cyclopropane toward conjugative interaction is born out in the relevant compounds by a shift of the ^1L_a ($\pi\pi^*$) absorption band: from acenaphthene to naphthocyclobutane (**2**) the red shift amounts to only 300 cm^{-1}, whereas in the naphthocyclopropane (**12**) the ^1L_a band is shifted by 1500 cm^{-1}.[45] A natural orbital correlation diagram[46] reveals an intended correlation of a nonbonding biradical π orbital with a σ^* orbital; thus, it is not surprising that the activation barrier for fission of the peri σ bond in the lowest $\pi\pi^*$ excited state (^1L_b) is higher for **2** than for **12** or **16**.

Conclusions

Each of several different products can be obtained in high yield from the azo compound **1** by choosing the appropriate conditions for the formation and the subsequent reactions of the biradical intermediate 1,4-perinaphthadiyl (b). The combined results of low-temperature spectroscopy, flash photolysis, and product analyses are rationalized in terms of Scheme II in which both the singlet and the triplet state of b appear as true, kinetically distinct intermediates. The reactions of b are mainly controlled by three variables: (i) the method of initiating the reaction—pyrolysis, direct photolysis, or sensitization of **1**—which determines the multiplicity of b when it is initially formed; (ii) the temperature, which influences the relative efficiency of three competing decay channels from ^{1}b—low temperatures favoring the nonactivated ISC to ^{3}b; (iii) the partial pressure of oxygen, which traps ^{3}b and catalyzes ISC from ^{1}b.

The seemingly minor difference in structure between the tetramethylene-bridged naphthoquinodimethane b and the trimethylene-bridged derivatives c and d has a very profound influence on the reactivity. The singlet state of d was found to be too short-lived to react with oxygen or to undergo ISC even at low temperature.[8] This work has provided evidence that the singlet biradical ^{1}b has a lifetime on the order of 1 ns at room temperature, sufficient for intermolecular reactions and spontaneous ISC to ^{3}b to compete with ring closure to naphthocyclobutane (**2**). Further work is aimed toward a direct detection of ^{1}b. The factors responsible for the stabilization of ^{1}b are open to question.

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Registry No. **1**, 52720-26-0; **1**-d_2, 113349-56-7; **2**, 32624-91-2; **3**, 17935-66-9; **4**, 113274-50-3; **5**, 113274-54-7; **6**, 113274-51-4; **7**, 72885-94-0; **8**, 66888-63-9; **9**, 113274-48-9; **10**, 113274-49-0; b, 52720-27-1; O_2, 7782-44-7; phenalene, 203-80-5; 1-phenalenone, 548-39-0; 1-acetonaphthone, 941-98-0; 2,3-dihydro,1,2,3-metheno-1*H*-phenalene-*2,10*-d_2, 113274-52-5; cyclohepta[*de*]naphthalene, 208-20-8; 1*H*,4*H*-1,4-ethenonaphtho[1,8-*de*][1,2]dioxepin, 113274-53-6; 7,8,15,16-tetrahydro-7,16:8,15-diethenocyclodeca[1,2,3-*de*:6,7,8-*d′e′*]dinaphthalene, 81293-14-3.

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Acid-Catalyzed Nucleophilic Aromatic Photosubstitution. A Reconsideration of Protonation in Excited States of Nitrobenzenes[†]

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Abstract: 3-Bromonitrobenzene is photosubstituted inefficiently but cleanly by chloride ion to give 3-chloronitrobenzene. The photosubstitution is catalyzed by hydronium ion; the limiting quantum yield of 0.021 at infinite [H^+] and 3.0 M [Cl^-] is only 2-fold higher than the quantum yield (0.011) of the uncatalyzed photosubstitution at 3.0 M [Cl^-]. The limiting quantum yield at infinite chloride ion concentration with no added acid is also 0.021. That 2-propanol does not intervene on the photosubstitution pathway to cause photoreduction indicates that radical intermediates are not involved, and the absence of deuterium incorporation on the aromatic ring accompanying photosubstitution indicates that the catalysis does not involve formation of a dihydrobenzene intermediate. The reaction appears to be an example of the so-called $S_N2\ ^3Ar^*$ mechanism and the catalysis to be a manifestation of protonation of the $^3\pi,\pi^*$ state, which is the higher energy triplet state in 3-bromonitrobenzene.

Elucidating the mechanisms of nucleophilic aromatic photosubstitution reactions continues to occupy the attention of photochemists.[1-14] A mechanistic classification scheme put forward by Havinga and co-workers[2,15] for these reactions rationalizes the preference for substitution meta to a nitro group in a π,π^* triplet nitrophenyl ether. A recent supplement to this scheme attributes

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[†] Dedicated to the memory of Douglas Phelps Susens.

[‡] Deceased April 17, 1987.

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