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Free-Radical Reactions of a [3.1.1]Propellane, 2,4-Methano-2,4-didehydroadamantane

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2,4-Methano-2,4-didehydroadamantane (**1**), a prototype small propellane, readily added disulfides and carbon tetrachloride across the central bond to give the corresponding 2,4-disubstituted 2,4-methanoadamantanes. Methyl phenyl disulfide as well as mixtures of dimethyl disulfide and diphenyl disulfide produced 2-(methylthio)-4-(phenylthio)-2,4-methanoadamantane (**4**) in addition to the symmetrical disulfides, 2,4-bis(methylthio)-2,4-methanoadamantane (**2**) and 2,4-bis(phenylthio)-2,4-methanoadamantane (**3**). The simultaneous formation of **2**, **3**, and **4** provides strong evidence that these reactions are indeed free-radical chain processes. Carbon tetrachloride, when present in an excess over **1**, generated a strong ESR signal corresponding to the 4-substituted 2,4-methano-2-adamantyl radical (**5**). The structure of this radical was confirmed by ESR of the radical derived from 2,4-methano-2,4-didehydroadamantane-*11,11-d*$_2$ (**1a**). The ESR signal appeared only when carbon tetrachloride was present in an excess over **1**, which indicated that **1** was a very efficient free-radical trap. Propellane **1** spontaneously reacted with α-phenyl-*N-tert*-butylnitrone, a spin-trapping agent, and *p*-benzoquinone, an electron-deficient olefin. The former reaction led to the corresponding nitroxide radical, and the latter one gave 4-methyleneadamantane-2-spiro-7′-bicyclo[4.1.0]hept-3′-ene-2′,5′-dione (**9**), most probably via a diradical intermediate. The behavior of **1** in all these reactions is consistent with the partial diradical character of this small propellane and suggests the term "diradicaloid" for such species.

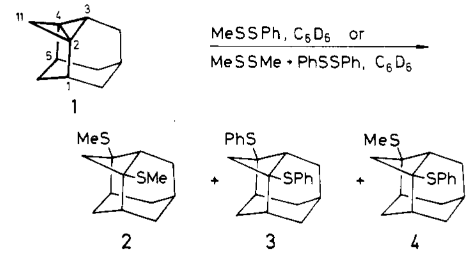
Propellanes possessing inverted carbon atoms readily react with molecules that can be relatively easily cleaved to free radicals.[1–8] Such molecules add across the bond between inverted carbon atoms. Thus, the parent [1.1.1]propellane was reported to spontaneously react with bromotrichloromethane, carbon tetrachloride, diphenyl disulfide, diphenyl diselenide, iodine,[1] and thiophenol[2] to give the corresponding 1,3-disubstituted bicyclo[1.1.1]pentanes. 2,4-Propano[1.1.1]propellane reacted in an analogous manner with thiophenol,[2] carbon tetrachloride, tri-*n*-butyltin hydride, and slowly with bromochloromethane.[3] Carbocyclic [3.1.1]propellanes, such as 2,4-methano-2,4-didehydroadamantane[4] and 2,6-methano-2,6-didehydronorbornane,[5] readily added carbon tetrachloride, tosyl chloride, and thiophenol across the central bonds. An oxa[3.1.1]propellane reacted analogously with ethanethiol.[6] 2,3-Methano-2,4-didehydroadamantane, an unsymmetrical [4.1.1]propellane,[7] as well as a dibenzo-[4.1.1]propellane[6,8] reacted with dimethyl disulfide,[7] a variety of thiols, and bromotrichloromethane[6] to give addition across the central bonds. No rearranged product was detected in any of these reactions, though small amounts of dimers and oligomers were occasionally observed.

These reactions were referred to as "probably"[2] or "almost certainly"[1] free-radical chain processes. However, no real proof has ever been offered for this assertion. Moreover, the product structures are also consistent with concerted additions across the propellane central bonds, as Barton recently pointed out.[9] Bearing in mind the unusual nature and chemical behavior of the bond between inverted carbons,[1–8,10–12] such an alternative possibility cannot be discounted.

In the present paper we clearly demonstrate that, at least, some of the above additions across the propellane central bonds do involve free-radical intermediates and are indeed free-radical chain processes.

Results and Discussion

Scheme I



Both dimethyl disulfide (DMDS) as well as diphenyl disulfide (DPDS) spontaneously added at room temperature across the central bond in propellane **1** to give 2,4-bis(methylthio)-2,4-methanoadamantane (**2**) and 2,4-bis(phenylthio)-2,4-methanoadamantane (**3**), respectively

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† Dr. Zdenko Majerski deceased August 28, 1988.

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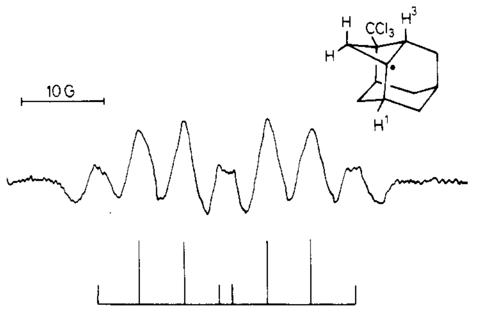
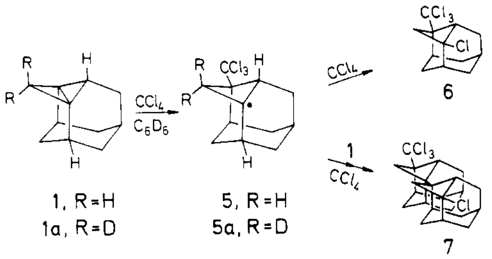


Figure 1. ESR spectrum of the 2,4-methano-2-adamantyl radical **5**.

Scheme II



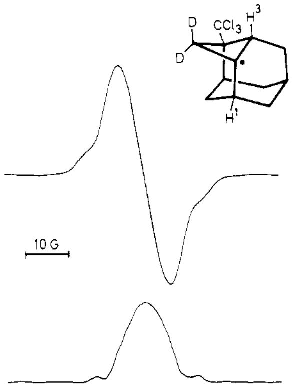
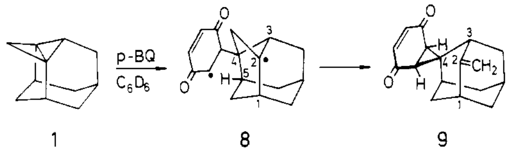


Figure 2. ESR spectrum of the 2,4-methano-2-adamantyl-*11,11*-d_2 radical **5a** recorded in the first (top) and the second (bottom) harmonic.

Scheme III



(Scheme I). Methyl phenyl disulfide, however, produced under the same conditions, 2-(methylthio)-4-(phenylthio)-2,4-methanoadamantane (**4**) as the major product, in addition to the symmetrical disulfides **2** and **3** (the ratio of **2**:**3**:**4** was determined to be 1:1:3 by ^{13}C NMR). The same three products were formed by treatment of **1** with mixtures of DMDS and DPDS. As expected[13] DPDS was more reactive than DMDS. A mixture of 1 equiv of DMDS and 1 equiv of DPDS reacted with 1 equiv of propellane **1** to give a 4:1 mixture of **3** and **4** (by ^{13}C NMR, disulfide **2** could barely be detected). However, a mixture of 4 equiv of DMDS and 1 equiv of DPDS produced disulfides **2**, **3**, and **4** in a ratio of 2:1:2, respectively.

These results clearly show that the reactions of disulfides with small propellanes, such as **1**, are indeed free-radical chain processes. The memory effect observed in the methyl phenyl disulfide reaction is consistent with the caged intermediary radical pairs. Such intermediates should preferably collapse to the corresponding disulfides.

Attempts to detect free-radical intermediates in the reaction of **1** with DMDS by ESR spectroscopy were unsuccessful at both room temperature and −80 °C. This is not surprising since bimolecular radical displacements at -SS- bonds are very rapid (e.g., $k = 2 \times 10^6$ M^{-1} s^{-1}).[14] In contrast, our attempt to detect free radicals in the reaction of **1** with carbon tetrachloride was quite fruitful. This reaction is known to produce 2-chloro-4-(trichloromethyl)-2,4-methanoadamantane (**6**), which is greater than 95% pure[4] (Scheme II). When carbon tetrachloride was added at room temperature in excess to a solution of **1** in benzene-d_6, a strong ESR signal appeared after a short induction period. The splitting pattern (Figure 1) indicated that the unpaired electron was coupled with four adjacent hydrogen atoms. Three splitting constants were approximately 5 G, while the fourth one was nearly 15 G. Such a coupling is consistent with the structure of the 2,4-methano-2-adamantyl free radical **5**. To confirm this hypothesis, we prepared a specifically deuteriated isotopomer of **1**, 2,4-methano-2,4-didehydroadamantane-*11,11*-d_2 (**1a**, R = D),[4] and studied its carbon tetrachloride reaction by ESR spectroscopy. The signal of the resulting free radical is shown in Figure 2. The splitting pattern is consistent with the structure of the 2,4-methano-2-adamantyl-*11,11*-d_2 radical **5a**. The two deuterium couplings are reduced by a factor of 6.5[15] in comparison with the corresponding couplings (5 and 15 G, associated with "CH$_2$" hydrogens) of the free radical derived from the nondeuteriated propellane **1**, while the other two remained the same.

Consequently, propellane **1** reacts with carbon tetrachloride by a free-radical process to give a 4-substituted 2,4-methano-2-adamantyl radical in the initial step. Since the trichloromethyl radical is more stable than the chloro radical,[16] the former is almost certainly the chain-carrying species, and, consequently, the substituent in the intermediary radical is the trichloromethyl group. It should be pointed out that the benzene-d_6 solutions of neither propellane **1** nor carbon tetrachloride showed any ESR signal prior to the reaction. When carbon tetrachloride was added in small, successive portions, no ESR signal appeared until the carbon tetrachloride was in an excess over propellane **1**. This is strong evidence that **1** acts as a very efficient free-radical trap. The ^{13}C NMR spectrum of the product obtained by such a successive addition of carbon tetrachloride to a benzene-d_6 solution of **1** showed the presence of 10–15% of byproducts, presumably dimers **7** and the derived oligomers (Scheme II). The reaction is initiated either by traces of free radicals present in the carbon tetrachloride solution or, perhaps, by the propellane itself. Attempts to trap the intermediary free radical by a spin-trapping agent, such as α-phenyl-*N*-*tert*-butyl-

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(12) (a) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985–1001 and 1001–1012. (b) Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 4133–4139. (c) Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227–1233. (d) Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591–599. (e) Messmer, R. P.; Schultz, P. A. *J. Am. Chem. Soc.* **1986**, *108*, 7407–7408. (f) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773–778. (g) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779–786. (h) Pierini, A. B.; Reale, H. F.; Medrano, J. A. *THEOCHEM* **1986**, *148*, 109–118. (i) Zilberg, S. P.; Ioffe, A. I.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 358–364.

(13) The S–S bond energy in DPDS is only 20–26 kcal/mol, while the bond energy of the S–S linkage in DMDS is 67–73 kcal/mol.[14]

(14) Field, L. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum Press: New York, 1977; Chapter 7.

(15) $\mu_H \cdot I_D / \mu_D \cdot I_H$.

(16) Huyser, E. S. *Free Radical Chain Reactions*; Wiley: New York, 1970; pp 148–151.

nitrone (PBN) led to a rapid reaction of PBN with 1 to give the corresponding phenyl *tert*-butyl nitroxide free radical (by ESR). This indicates that 1 probably possesses free-radical character to a certain extent.

PBN is a species containing an electron-deficient carbon–nitrogen double bond. The high reactivity of propellane 1 toward PBN prompted us to study the reaction of 1 with *p*-benzoquinone (p-BQ), an electron-deficient olefin (Scheme III). The reaction at room temperature was instantaneous and vigorous. The ^{13}C NMR spectrum of the crude product indicated the presence of a single product in addition to small amounts of polymeric material. The product was purified by column chromatography and identified as 4-methyleneadamantane-2-spiro-7′-bicyclo[4.1.0]hept-3′-ene-2′,5′-dione (9) by ^{13}C NMR, ^{1}H NMR, IR, and mass spectra. Similar reactions of the parent [1.1.1]propellane with electron-deficient alkenes and alkynes were recently reported by Wiberg.[17]

The mechanism of this reaction most probably involves the initial interaction of an electron-rich outside lobe of the propellane central bond orbitals with one of the two electron-deficient olefinic bonds in p-BQ. The resulting 2,4-methano-2-adamantyl diradical 8 rearranges to the corresponding, more stable,[18,19] 4-substituted 2-methylene-4-adamantyl diradical, which then closes up the cyclopropane ring to give 9. This mechanism is consistent with a significant electron density outside the inverted carbons as indicated by the results of both experimental[11] and theoretical[12] studies on small propellanes. It is also in good agreement with the mechanism proposed for the parent [1.1.1]propellane reactions with electron-deficient alkenes and alkynes.[17] Moreover, the analogous reaction of 1 with the double bond in PBN was shown to involve a free-radical intermediate (vide supra). The reaction could, in principle, also proceed via a zwitterionic intermediate corresponding to diradical 8. However, such an intermediate would contain the 2,4-methano-2-adamantyl cation moiety, which should readily rearrange to give a mixture of products,[4] rather than to produce only 9.

The adamantane nucleus and the *p*-benzoquinone ring in the product could be either anti or syn to each other. However, only one isomer was formed (most probably anti). This is consistent with the expected steric repulsion between the hydrogen atom attached to the adamantane carbon-5 and the *p*-benzoquinone ring.

In conclusion, 2,4-methano-2,4-didehydroadamantane (1), a prototype small propellane, readily reacts with disulfides and carbon tetrachloride as well as with *p*-benzoquinone via free-radical intermediates. The former two reactions are free-radical chain processes, while the latter one, most probably, involves diradicals. Small propellanes, such as 1, appear to have partial diradical character and, hence, may be considered as "diradicaloids".

Experimental Section

The purity of all compounds was determined by GC and/or ^{13}C NMR. ^{13}C NMR and ^{1}H NMR spectra were acquired with a JEOL FX 90Q spectrometer, IR spectra were recorded with a Perkin-Elmer 297 spectrophotometer, and mass spectra were obtained on a Varian CH-7 spectrometer. ESR spectra were recorded on a Varian E-109 spectrometer operating at X-band frequency and 100-kHz field modulation. The samples were placed in ESR tubes (without special treatment) and measured at room temperature if not specified otherwise. GC analyses were carried out on a Varian Aerograph 1800 gas chromatograph. Melting points were determined in a Thiele apparatus and were uncorrected. Carbon tetrachloride was of spectroscopic grade; all other chemicals were of commercial reagent grade.

Propellane 1 was prepared in 70% yield by pyrolysis (180 °C, 0.02 mmHg) of the dry tosylhydrazone salt derived from 4-methylene-2-adamantanone (162 mg, 1 mmol) as described previously.[4] The product was trapped in a liquid nitrogen cooled trap and dissolved in dry benzene-d_6 or toluene-d_8 (0.4 mL) under a dry nitrogen atmosphere. The purity of 1 was checked by ^{13}C NMR prior to further experiments.

Reactions of 1 with Disulfides. Dimethyl disulfide, DMDS (107 mg, 1.14 mmol), was added to a benzene-d_6 solution of 1 (prepared from 375 mg, 1.14 mmol of the tosylhydrazone) in an NMR tube at room temperature. The purity of the product was greater than 98% (by ^{13}C NMR). The solvent was evaporated and the product was distilled in a Kugelrohr apparatus (206–208 °C/15 mmHg) to give pure 2 (171 mg, 89%): ^{13}C NMR ($CDCl_3$) δ 48.5 (s, 2 C), 46.2 (d, 1 C), 40.1 (dd, 1 C), 35.1 (t, 1 C), 35.0 (d, 2 C), 32.5 (t, 2 C), 28.2 (t, 1 C), 25.4 (d, 1 C), 11.2 (q, 2 C); ^{1}H NMR ($CDCl_3$) δ 2.5–2.2 (m, 2 H, and a clear doublet δ 2.4, J = 9 Hz, 1 H), 2.2–1.3 (m, 10 H, with a sharp singlet δ 2.0, 6 H, and a clear doublet δ 1.7, J = 9 Hz, 1 H); IR (film) 2900, 2840, 1440, 1255, 1100, 1060, 930, 910 cm^{-1}; MS, m/z (relative intensity) 240 (M$^+$, trace), 193 (100), 145 (19), 91 (25). Anal. Calcd for $C_{13}H_{20}S_2$: C, 64.94; H, 8.38. Found: C, 64.80; H, 8.74.

The reaction of 1 with DMDS was also performed in the ESR cavity at room temperature (in benzene-d_6) and at −80 °C (in toluene-d_8). No ESR signal was detected in either of these experiments.

Diphenyl disulfide, DPDS (235 mg, 1.08 mmol), was added to a benzene-d_6 solution of 1 (obtained from 355 mg, 1.08 mmol of the tosylhydrazone) as described above. ^{13}C NMR spectrum of the crude product mixture showed the presence of only disulfide 3 (90%) and DPDS (10%). Purification by column chromatography on silica gel with pentane–benzene (9:1) through benzene as the eluent followed by recrystallization from 10% benzene in pentane afforded pure 3 (272 mg, 99%): mp 102–104 °C; ^{13}C NMR ($CDCl_3$) δ 135.5 (d, 4 C), 131.8 (s, 2 C), 128.6 (d, 4 C), 128.1 (d, 2 C), 51.7 (s, 2 C), 47.5 (d, 1 C), 43.6 (dd, 1 C), 35.1 (t, 1 C), 34.8 (d, 2 C), 32.3 (t, 2 C), 27.6 (t, 1 C), 25.5 (d, 1 C); ^{1}H NMR ($CDCl_3$) δ 7.1 (br s, 10 H), 2.50 (d, J = 9 Hz, 1 H), 2.4–1.2 (m, 12 H, and a clear doublet δ 1.49, J = 9 Hz, 1 H); IR (KBr) 3060, 2990, 2900, 2840, 1565, 1465, 1430, 1215, 1060, 940, 740, 685 cm^{-1}; MS, m/z (relative intensity) 255 (100, M$^+$ − SPh), 145 (10), 91 (18). Anal. Calcd for $C_{23}H_{24}S_2$: C, 75.78; H, 6.63. Found: C, 75.64; H, 6.75.

Methyl phenyl disulfide[20] (156 mg, 1.0 mmol) was added at room temperature to a benzene-d_6 solution of 1 (prepared from 378 mg, 1.21 mmol of the tosylhydrazone). The ^{13}C NMR spectrum of the crude product showed the presence of three components, 2, 3, and 4, in a ratio of 1:1:3. The solvent was evaporated and the major product (4) was isolated from the crude mixture (174 mg) by column chromatography on silica gel with pentane–benzene (4:1 through 2:3) as the eluent. Disulfide 4 (100 mg) was distilled in a Kugelrohr apparatus (72–76 °C/0.04 mmHg) prior to the analyses: ^{13}C NMR ($CDCl_3$) δ 135.5 (d), 132.4 (s), 128.7 (d), 128.1 (d), 51.2 (s), 48.9 (s), 46.5 (d), 41.7 (dd), 35.2 (t), 35.0 (d), 34.5 (d), 32.5 (t), 32.2 (t), 27.8 (t), 25.3 (d), 10.9 (q); ^{1}H NMR ($CDCl_3$) δ 7.5–7.2 (m, 5 H), 2.5–1.2 (m, 17 H, with a sharp CH_3 singlet δ 1.82 and two clear doublets δ 2.45, J = 9.1 Hz and δ 1.61, J = 9.1 Hz); IR (film) 3040, 3020, 2900, 2840, 1580, 1470, 1430, 1255, 1095, 1060, 930, 740, 685 cm^{-1}; MS, m/z (relative intensity) 302 (M$^+$, trace), 255 (34), 193 (100), 145 (16), 91 (24).

Mixtures of DMDS and DPDS were added to a benzene-d_6 solution of 1 in an NMR tube at room temperature. The product ratios were determined by ^{13}C NMR. When 1 equiv of propellane 1 was treated with 1 equiv of DMDS and 1 equiv of DPDS a 4:1 mixture of 3 and 4, respectively, was obtained. A mixture of 4 equiv of DMDS and 1 equiv of DPDS gave, however, a 2:1:2 mixture of 2, 3, and 4, respectively.

ESR Studies. Reaction of 1 with Carbon Tetrachloride. A solution of 1 in benzene-d_6 was treated in an ESR tube with

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[17] Wiberg, K. B.; Waddell, S. T. *Tetrahedron Lett.* **1987**, *28*, 151–154.

[18] The 2,4-methanoadamantane skeleton was calculated to be 34 kcal/mol more strained than the adamantane skeleton by the molecular mechanics method with the MM2 force field.[19]

[19] Burkert, U., private communication.

[20] McAllan, D. T.; Cullum, T. V.; Dean, R. A.; Fidler, F. A. *J. Am. Chem. Soc.* **1951**, *73*, 3627–3632.

carbon tetrachloride at room temperature. When carbon tetrachloride was added in excess (one large portion) over 1, a clear ESR signal appeared after a 10–20-min induction period. The intensity of the signal increased with time. However, when carbon tetrachloride was added in small, successive portions, no ESR signal appeared as long as 1 was in an excess over carbon tetrachloride. The benzene-d_6 solutions of either 1 or carbon tetrachloride showed no ESR signal at maximum sensitivity.

Reaction of 1 with α-Phenyl-*N*-*tert*-butylnitrone (PBN). A 0.005 M solution of PBN in benzene-d_6 was added to a benzene-d_6 solution of 1 (0.3 mmol, 0.2 mL) in an ESR tube at room temperature. The immediate appearance of a strong ESR signal indicated that a free radical (spin-trap adduct) was formed. The splitting pattern was typical for the phenyl *tert*-butyl nitroxide free radical. As expected, the hyperfine coupling of the proton doublet and the nitrogen triplet gave no useful information on the structure of the attached radical.[21,22]

Reaction of 1 with *p*-Benzoquinone. Freshly sublimed *p*-benzoquinone, p-BQ (110 mg, 1.02 mmol), was added at room temperature to a benzene-d_6 solution of 1 (obtained from 365 mg, 1.1 mmol of the tosylhydrazone). The reaction was rather vigorous. The ^{13}C NMR spectrum of the crude product showed the presence of 9, p-BQ, and small amounts of a polymeric material. The solvent was evaporated and the product was purified by column chromatography on neutral alumina (activity II/III) with methylene chloride as the eluent to give 9 (138 mg, 70%): ^{13}C NMR ($CDCl_3$) δ 193.7 (s), 193.0 (s), 152.7 (s), 140.9 (d), 140.7 (d), 104.0 (t), 48.2 (s), 40.8 (t), 39.5, 39.3, 38.4, 38.1, 37.75, 37.71, 37.4, 35.7 (t), 27.2 (d); ^{1}H NMR ($CDCl_3$) δ 6.66 (s, 2 H), 4.57 (d, J = 1.5 Hz, 1 H), 4.32 (d, J = 1.5 Hz, 1 H), 2.9–1.3 (m, 14 H, with two doublets δ 2.4, J = 6.4 Hz and δ 2.2, J = 6.4 Hz); IR (film) 3060, 2910, 2850, 1660, 1600, 1440, 1295, 1090, 880 cm^{-1}; MS, m/z (relative intensity) 254 (M^+, 100), 91 (67).

Acknowledgment. We thank Professor P. J. Stang for critical reading of the manuscript. This research was supported by a grant from the Research Council of the Republic of Croatia (SIZZ) and by the U.S.–Yugoslav Joint Fund for Scientific and Technological Cooperation, in cooperation with the NSF under Grant PN-531.

Registry No. 1, 73586-31-9; 2, 118248-39-8; 3, 118248-40-1; 4, 118248-41-2; DMDS, 624-92-0; DPDS, 139-66-2; methyl phenyl disulfide, 14173-25-2.

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[21] These couplings are known to be quite insensitive to the structure of attached radical.[22]

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Free-Radical Nitration of Naphthalene with Nitrogen Dioxide in CCl_4 and Implications for Environmental Nitrations

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The nitration of naphthalene (NAP) with nitrogen dioxide in carbon tetrachloride occurs via a free-radical mechanism, involving metastable adducts of NAP and 2–4 mol of NO_2 per mole of NAP. This free radical nitration system is characterized by (1) low 1-nitronaphthalene/2-nitronaphthalene (1NNAP/2NNAP) ratios and (2) the formation of unexpected dinitronaphthalene isomers, 1,3-dinitronaphthalene (1,3-diNNAP) and 2,3-dinitronaphthalene (2,3-diNNAP), at low conversions. There is strong steric repulsion of the nitro groups in the ORTEP drawing of the 2,3-diNNAP crystal structure (Figure 1). The elimination of HNO_2 from a postulated tetranitrotetrahydronaphthalene intermediate is, therefore, suggested to occur under kinetic control. The nitro substituent has a small activating effect toward free-radical nitration in 2NNAP while it has no noticeable effect in 1NNAP, contrasting sharply with conventional electrophilic nitration where the nitro substituent has a very strong deactivating effect. An ionic electrophilic reaction mechanism predominates in solvents of higher polarity and is subject to efficient acid catalysis. We suggest our conditions of free-radical nitration model the gas-phase atmospheric free-radical nitration of NAP, where low 1NNAP/2NNAP ratios and 1,3-diNNAP also have been reported. Thus, free-radical reactions might be responsible for producing some of the nitro-containing polycyclic aromatic hydrocarbon mutagens that are found in the environment.

The nitration of naphthalene (NAP) has been the subject of several studies that have contributed to our current knowledge of the mechanisms of the nitration of aromatic hydrocarbons.[1-14] However, the nitration of NAP by nitrogen dioxide[15] under free-radical conditions (e.g., neutral conditions in solvents of low polarity) has not been studied in detail. The literature contains a few reports on the nitration of NAP with nitrogen dioxide under various conditions, including the reaction of solid NAP with liquid N_2O_4[16] and the reaction of NAP with NO_2 in CH_2Cl_2[12,13,17] or in more polar solvents like acetonitrile[1] and sulfolane.[5-7] Barlas and his collaborators investigated the photochemical reactions of NAP with NO_2 in CCl_4,[18] but their studies were complicated by reactions of reactive intermediates with the solvent.

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