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); ^1H 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).

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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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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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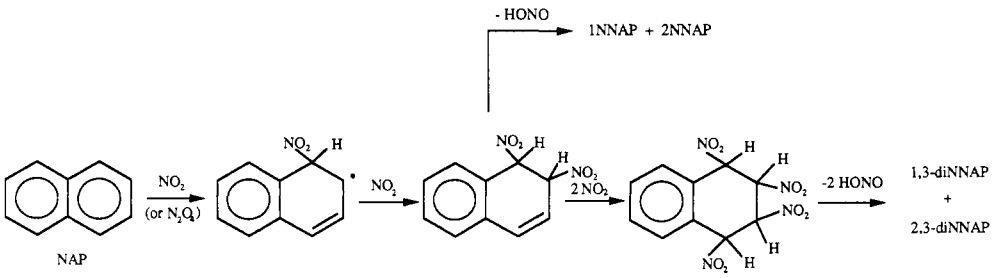
Scheme I



Recently, free-radical nitration of polycyclic aromatic hydrocarbons (PAH) has attracted the attention of the environmental community because of the identification of unexpected NO_2-PAH in samples of ambient particulate organic matter (POM)[19,20] that cannot be explained in terms of the classical ionic electrophilic mechanism of nitration. We have reported that the nitration of fluoranthene[21,22] and anthracene[23] by NO_2 in CCl_4 involves radical intermediates and, judged from the products obtained, models the nitrations that occur in the atmosphere. Therefore, we have undertaken a more complete study of the nitration of NAP with NO_2 in CCl_4.

Results and Discussion

The 1-Nitronaphthalene/2-Nitronaphthalene (1NNAP/2NNAP) Ratio. The 1-nitronaphthalene/2-nitronaphthalene (1NNAP/2NNAP) ratios obtained under several nitration conditions are illustrated in Table I. The reaction of NAP with liquid N_2O_4 at 18–20 °C has been reported to yield 1NNAP exclusively. The nitration of NAP with NO_2 in CCl_4 gives an 1NNAP/2NNAP ratio similar to that obtained in nitrations by the nitronium ion (or a strongly solvated modification thereof). It also affords a 1NNAP/2NNAP ratio markedly lower than that obtained with NO_2 in more polar solvents like sulfolane or acetonitrile. High 1NNAP/2NNAP ratios have also been reported for the nitration of NAP with NO_2 in CH_2Cl_2.[12,13,17] However, when 2,6-di-*tert*-butylpyridine (DTBP) is used as scavenger of acids[24] in CH_2Cl_2, a lower 1NNAP/2NNAP ratio (about 4) is obtained, and the reaction rate is also slower, comparable to that obtained in CCl_4. (DTBP does not significantly change the products when the nitration is carried out in CCl_4.) Thus, nitric and/or nitrous acid are efficient catalysts of an ionic nitration pathway in solvents more polar than CCl_4.

Table I. Nitration of Naphthalene under Different Conditions

reagent	solvent	temp[a]	1NN/2NN	ref
NO_2BF_4	sulfolane	25	10	1
NO_2BF_4	nitromethane	25	12	1
$C(NO_2)_4$	gas phase	300	1	1
NO_2	acetonitrile	25	24	1
NO_2	sulfolane	25	19	7
NO_2	CH_2Cl_2	*b*	24	17
NO_2	CH_2Cl_2[c]	25	4	*d*
NO_2	CCl_4	25	10	*d*
NO_2	CCl_4[c]	25	8	*d*
NO_2	CCl_4	50	4.5	*d*
NO_2	no solvent	18–20	*e*	16
HNO_3	H_3PO_4	25	5–6	15
HNO_3	AcOH	50	16	*f*
HNO_3	Ac_2O	50	8	*f*

[a] Degrees Celcius. [b] Room temperature. [c] 2,6-Di-*tert*-butylpyridine was added to scavenge nitric and nitrous acids. [d] This work. [e] Exclusive formation of 1-nitronaphthalene was reported. [f] Streitweiser, A., Jr.; Fahey, R. C. *J. Org. Chem.* **1962**, *27*, 2352–2355.

The Formation of Unusual Dinitronaphthalenes at Low Conversions. The most striking feature of the nitration of NAP with NO_2 in CCl_4 is the formation of the unexpected 1,3-dinitronaphthalene (1,3-diNNAP) and 2,3-dinitronaphthalene (2,3-diNNAP) even at low conversions. The formation of these dinitronaphthalenes in the nitration of NAP is unprecedented.

Under conditions of conventional electrophilic nitration, benzene reacts with HNO_3/H_2SO_4 about 10^9 times faster than does nitrobenzene.[25] Therefore, if dinitration of NAP were to occur by an electrophilic mechanism, the second nitro group would be expected to add to the unsubstituted ring of the nitronaphthalene. Furthermore, the nitro group is a meta director. The formation of 1,3-diNNAP and 2,3-diNNAP thus violates the well-established rules of conventional electrophilic nitration.

Mechanistic Considerations. A change in the nitration mechanism with changing solvents is suggested by two observations. Firstly, the 1NNAP/2NNAP ratio becomes lower as the solvent polarity is lowered or upon the addition of the nonnucleophilic base DTBP. Secondly, dinitronaphthalenes are not formed in the acid-catalyzed nitration of NAP by NO_2 in CH_2Cl_2.[12,13,17] With NO_2 in CCl_4, dinitronaphthalenes are formed at low conversions. The operation of an ionic electrophilic mechanism in CCl_4 can be ruled out because, under these conditions, the nitro

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(24) (a) Notice that nitrous acid is a byproduct. Nitrous acid is in equilibrium with dinitrogen trioxide and water. N_2O_4 disproportionates to nitric and nitrous acids in the presence of water. (b) The nitrations of fluoranthene[22] and anthracene[12,23] with NO_2 in CH_2Cl_2 also follow a different mechanism in the presence of small amounts of water.
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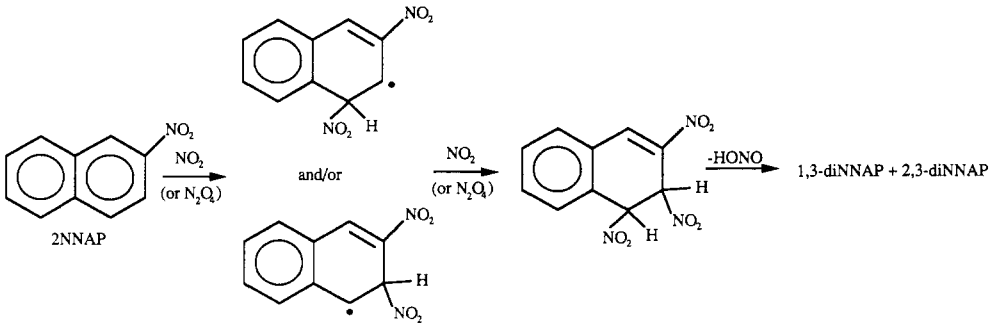
Table II. Distribution of Nitro- and Dinitronaphthalenes in the Nitration of Naphthalene and Nitronaphthalenes

							NNAP		diNNAP					
subst	solvent	reagent	temp[a]	time[b]	conv[c]	yield[c]	1	2	1,3	2,3	1,5	1,6	1,7	1,8
NAP[d]	CCl_4	NO_2[e]	25	24	12	95[f]	58	6	19	16				
NAP[g]	CCl_4	NO_2[e]	25	25	12	95[f]	57	6	19	18				
NAP[h]	CCl_4	NO_2[i]	50	15	7	95[f]	24	9	33	34				
NAP[j]	CCl_4	NO_2[k]	50	16	6	95[f]	31	7	31	31				
NAP[h]	CCl_4	NO_2[i]	50	39	9	95[f]	27	6	29	38				
2NNAP[d]	CCl_4	NO_2[e]	25	21	8	56			67	33				
1NNAP[l]	H_3PO_4	HNO_3	0								31			69
2NNAP[l]	H_3PO_4	HNO_3	0									42	52	

[a] Degrees Celcius. [b] Hours. [c] Percentage. [d] 2.0 M; 1.5 mL. [e] 2 M; 2.4 mL; concentration of NO_2 denotes total N(IV) in the equilibrium mixture of NO_2 and N_2O_4. [f] A small amount of a naphthoquinone and of a third dinitronaphthalene, identified as 1,4-dinitronaphthalene by a best-match algorithm provided with the Hewlett-Packard MS software, account for the remaining 5%. [g] 2.7 M; 1.5 mL. [h] 3.4 M; 1.3 mL. [i] 1 M; 2.5 mL. [j] 2.1 M; 2.0 mL. [k] 1 M; 1.5 mL. [l] Reference 26.

Scheme II



group is a meta director with strong deactivation. As can be seen in Table II, the diNNAP's substitution pattern obtained with NO_2 in CCl_4 contrasts sharply with those obtained by nitration of 1NNAP and 2NNAP with HNO_3/H_2SO_4.[26]

Many free-radical aromatic substitutions are facilitated by both electron-releasing and -withdrawing substitutents. Therefore, the product distributions of the nitration of 1NNAP and 2NNAP also were studied to investigate the possibility of a two-step free-radical nitration. At 25 °C, the reactivity of 1NNAP toward NO_2 is comparable to that of NAP whereas 2NNAP reacts about 8 times faster than does NAP. The nitration of 1NNAP to about 4% conversion yields a complex mixture of seven diNNAP's and four trinitronaphthalenes but was not investigated further. The nitration of 2NNAP yields 1,3-diNNAP and 2,3-diNNAP. Table II shows the product distribution of the nitration of NAP at 25 °C and 50 °C and of 2NNAP at 25 °C. The product distribution of the nitration of NAP remains unchanged up to about 15% conversion. Thus, the production of diNNAP's occurs too early in the nitration of NAP in CCl_4 for their formation to arise from further free-radical nitration of either 1NNAP or 2NNAP.

Schemes I and II show multi-step, radical addition–elimination mechanisms that explain the formation of the observed products from the reaction of NAP and 2NNAP with NO_2 in CCl_4, respectively. We proposed a similar mechanism for the nitration of fluoranthene under comparable conditions.[21,22]

As can be seen in Table II, the dinitronaphthalenes yields increase as the temperature is raised from 25 °C to 50 °C. This implies that the addition of NO_2 to the double bond of the newly formed styrene moiety has a larger activation energy than does the elimination of HNO_2 from it.

Although the adducts of two to four NO_2 groups to NAP (and the adducts to the naphthalene moiety of fluoranthene[21,22]) are not isolable, anthracene yields *cis*- and *trans*-9,10-dinitro-9,10-dihydroanthracene, due to the smaller aromatization energy of its middle ring.[23] The adducts of NO_2 and anthracene thus provide further indirect proof for our proposed multiple addition intermediates in the radical nitration of naphthalene and fluoranthene. Multiple addition intermediates of varying stability appear to be a common pattern in the radical nitration of PAH, contrasting sharply with electrophilic nitration where σ-complexes normally lose their acidic proton before nucleophilic capture can take place.

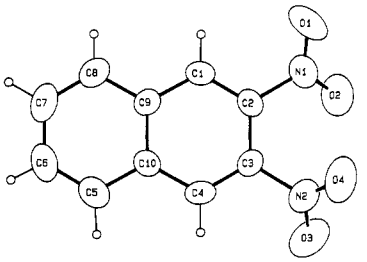


Figure 1. ORTEP drawing of the X-ray structure of 2,3-dinitronaphthalene showing the orientation of the nitro groups.

The nitrations of NAP and of 2NNAP with NO_2 in CCl_4 are synthetically useful and lead to two diNNAP's in one step. Previous syntheses of 2,3-diNNAP involved bromination–dehydrobromination of 1,2,3,4-tetrahydro-2,3-dinitronaphthalene[27] or of 1,2,3,4-tetrahydro-6,7-dinitronaphthalene,[28] both of which are not easily accesible starting materials. Existing methods for the synthesis of 1,3-diNNAP involve one of these multiple step routes: (a) the dinitration of 1-naphthol followed by transformation to the chloride and, finally, dehalogenation by Cu powder in molten organic acid;[29] (b) dinitration and cracking of

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the Diels–Alder adducts of naphthalene and hexachlorocyclopentadiene;[30,31] and (c) peracid oxidation of the corresponding diamine or nitroamine to 1,3-diNNAP.[32]

Kinetically Controlled Elimination. We have conducted a single-crystal X-ray study of 2,3-diNNAP to investigate the steric interactions at the sites of substitution. The ORTEP drawing of the crystal structure of 2,3-diNNAP shows strong steric hindrance (Figure 1). The nitro substituents are rotated significantly out of the best plane of the naphthalene ring system, forming dihedral angles of 33.0 (1)° (for N1) and 47.5 (1)° (for N2) with that plane. The two nitro groups best planes, calculated, including the nitro-substituted carbon atoms, intersect with a dihedral angle of 51.8 (2)°. Similar out-of-plane rotations of nitro substituents adjacent to each other on benzene rings occur in hexanitrobenzene,[33] 4-chloro-1,2-dinitrobenzene,[34] and 2,3,4,6-tetranitroaniline.[35] The naphthalene ring is measurably nonplanar, with an average deviation from the best plane of 0.009 (1) Å and a maximum deviation of 0.021 (2) Å for C3, one of the nitro-substituted carbon atoms. The two nitrogen atoms lie on either side of this plane, at distances of 0.150 (3) Å for N1 and 0.219 (3) Å for N2. Bond distances within the naphthalene nucleus exhibit the pattern of long and short values observed in 1,8-dinitronaphthalene[36] and 1,5-dinitronaphthalene,[37] as well as in naphthalene[38] itself. While the N1–O2 and N2–O4 distances within the nitro groups are normal at 1.230 (2) and 1.234 (2) Å, respectively, the N1–O1 and N2–O3 are shortened at 1.203 (2) and 1.196 (2) Å. Since none of the analogous compounds mentioned above exhibit this shortening, and since oxygen atoms O1 and O3 have the largest thermal parameters of the structure (B = 9.28 and 9.03 Å^2, respectively), we feel that this shortening is an artifact of the thermal motion.

The formation of the very unexpected vicinal dinitroaromatic hydrocarbons is characteristic of the NO_2/CCl_4 nitration system for both NAP and fluoranthene. (Fluoranthene yields 1,2-dinitrofluoranthene among other products.) We propose that these hindered vicinal dinitro species arise from the kinetically controlled regiospecific elimination of nitrous acid from the metastable multiple addition intermediates. Elimination of nitrous acid in the tetranitrotetrahydronaphthalene intermediate is likely to start by the weakening of one of the C–N bonds at the benzylic positions, where a partial positive charge can be stabilized by resonance, as suggested by the presence of only very small amounts of a third dinitronaphthalene, identified as 1,4-diNNAP (Table II).

Environmental Relevance. It has been found that two- to four-ring PAH produced from gasoline-fueled vehicles occur mainly in the gas phase.[39] Nitrogen dioxide is also an important atmospheric pollutant produced by a variety of anthropogenic activities including fossil fuel combustion and biomass burning. We suggest that our reaction conditions model free-radical gas-phase atmospheric reactions of NAP and NO_2, and probably other PAH as well.[21–23] Mutagenic nitro- and dinitronaphthalenes[40,41] are known to be produced in the atmosphere, and low 1NNAP/2NNAP ratios[19] and 1,3-diNNAP[20] have been reported in urban ambient air, just as we have observed in CCl_4.

Experimental Section

Materials and Methods. Carbon tetrachloride (Mallinckrodt Analytical Reagent) was dried over molecular sieves. Methylene chloride (Mallincrodt ChromAr HPLC) was dried over sodium sulfate, distilled, and stored over molecular sieves. Solvents were thoroughly purged with dry nitrogen prior to use. Naphthalene (Fischer, scintillation grade) and 2,6-di-*tert*-butylpyridine (Aldrich) were used without further purification. Dinitrogen tetroxide (MCB) was distilled until a pure white solid was obtained, indicating that it was freed of lower nitrogen oxides. The purified N_2O_4 was stored in bulbs with teflon stopcocks over phosphorus pentoxide (Alfa). The ^{1}H NMR spectra were recorded in $CDCl_3$ on a 100-MHz NR Bruker spectrometer, with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield from TMS. Yields and product distributions were determined by GC on a Varian 3700 gas chromatograph with a 30-m DB-5 J&W capillary column and interfaced to a Varian CDS 111 integrator. Relative response factors to the FID detector were determined with the purified compounds. GC/MS analyses were conducted on a Hewlett-Packard 5970 STET with a 20-m DB-17 J&W capillary column. Separation of dinitronaphthalenes can be easily performed by silica gel column chromatography using hexane–methylene chloride mixtures. 1,3-Dinitronaphthalene elutes prior to 2,3-dinitronaphthalene in all chromatographic methods tried here.

General Nitration Protocol. A solution of NO_2 in CCl_4 (1.5–2.5 mL; 1–2 M) was added under nitrogen to a solution of naphthalene or nitronaphthalene in CCl_4 (1.3–2.0 mL; 2.0–3.4 M) in a septum-capped vial via a syringe. A similar protocol was used for the run in methylene chloride, where the solution of NO_2 was spiked with ca. 2% 2,6-di-*tert*-butylpyridine (relative to the moles of naphthalene employed) prior to mixing with the solution containing the naphthalene. A similar protocol was used to determine the relative reactivity of 1- and 2-nitronaphthalene toward nitrogen dioxide, which was calculated by GC without an internal standard and has therefore to be regarded as semiquantitative.

X-ray Experimental. Data were collected from a pale yellow crystal 0.15 × 0.18 × 0.72 mm on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Crystal data are $C_{10}H_6N_2O_4$, FW = 218.2, monoclinic space group $P2_1/n$, a = 6.879 (2) Å, b = 14.802 (2) Å, c = 9.5511 (11) Å, β = 91.81 (2)°, V = 972.0 (5) Å^3, Z = 4, D_c = 1.491 g cm^{-3}, μ = 1.1 cm^{-1}, T = 22 °C. Scan rates varied, 0.50–4.0°/min, for $\omega - 2\theta$ scans within $1° < \theta < 30°$, in one quadrant. Of 2832 unique data, 1732 had $I > \sigma(I)$ and were used in the refinement. Data reduction included corrections for background, Lorentz, and polarization effects. The structure was solved by direct methods and refined by full-matrix least-squares methods based on F with weights $w = \sigma^{-2}(Fo)$, using the Enraf-Nonius SDP. Non-hydrogen atoms were treated anisotropically. Hydrogen atoms were located by ΔF and were refined isotropically. At convergence, R = 0.072 for 169 variables, and the maximum residual density was 0.34 e Å^{-3}. Coordinates and further data are given in the supplementary material.

1,3-Dinitronaphthalene: ^{1}H NMR (100 MHz, $CDCl_3$) δ 9.07 (d, 1 H, J(2,4) = 2 Hz, H2), 8.98 (d, 1 H, H4), 8.64 (br d, 1 H, J(7,8) = 8 Hz, H8), 8.21 (br d, 1 H, J(4,5) = 8 Hz, H4), 7.98 (m, 1 H, H7), 7.82 (m, 1 H, H5); MS, m/z (relative intensity) 218 (M^+,

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80), 201 (73), 172 (26), 171 (30), 142 (14), 127 (16), 126 (100), 125 (33), 114 (44), 113 (20).

2,3-Dinitronaphthalene: ^{1}H NMR (100 MHz, $CDCl_3$) δ 8.46 (br s, 2 H, H1), 7.97-8.18 (m, 2 H, H6), 7.65-7.95 (m, 2 H, H7); MS m/z (relative intensity) 218 (M^+, 100), 188 (14), 160 (4), 144 (19), 130 (27), 127 (7), 126 (63), 115 (9), 114 (88), 113 (22).

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Supplementary Material Available: Tables with full coordinates, bond distances, bond angles, and anisotropic thermal parameters for 2,3-dinitronaphthalene (8 pages). Ordering information is given on any current masthead page.

Synthesis and Kinetic Study of Antioxidant Activity of New Tocopherol (Vitamin E) Compounds

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New tocopherol (vitamin E) compounds (5,7-diethyltocol (**3**), 5,7-diisopropyltocol (**4**), 7-*tert*-butyl-5-methyltocol (**5**), and 8-*tert*-butyl-5-methyltocol (**6**)) have been synthesized by condensation of isophytol with the corresponding alkylhydroquinone. The second-order rate constants, k_s, for the reaction of 10 kinds of tocopherol derivatives including α-, β-, γ-, and δ-tocopherols with substituted phenoxyl radical in ethanol have been measured in the temperature range 10.0-35.0 °C, with a stopped-flow spectrophotometer, as a model reaction of tocopherols with unstable free radicals (LOO•, LO•, and HO•) in biological systems. The result indicates that the rate constants, k_s, increase as the total electron-donating capacity of the alkyl substituents on the aromatic ring increases. For the tocopherol derivatives, log k_s was found to correlate roughly with the sum of the Hammett's σ constants ($\Sigma\sigma$) or the Brown's σ^+ constants ($\Sigma\sigma^+$), but the two cases could not be distinguished. Half-peak oxidation potentials ($E_{p/2}$) for tocopherol compounds have also been measured by using a cyclic voltammetry technique. The log of the second-order rate constants, k_s, obtained for tocopherols was found to correlate with their half-peak oxidation potentials ($E_{p/2}$). The antioxidant activities of tocopherol derivatives **2-5** having two alkyl substituents, such as methyl, ethyl, isopropyl, and *tert*-butyl groups, at the ortho positions of the OH group are similar to each other, suggesting that the effect of steric hindrance on the reaction rate is small. Further, the reactivities of these tocopherols **2-5** are about half that of α-tocopherol. From detailed analysis of the temperature dependence of k_s values of the tocopherols, the activation energy, E_{act}, for the reaction has been determined. The observed activation energies were found to be related linearly to the half-peak oxidation potentials. From the results, the property of the transition state in the above free radical scavenging reaction by tocopherols has been discussed. Electron spin resonance measurements were performed for the tocopheroxyl radicals **3-6** in toluene, and the proton hyperfine coupling constants and g_{iso} values were determined.

Introduction

Vitamin E compounds (α-, β-, γ-, and δ-tocopherols) are well known as scavengers of active free radicals (LOO•, LO•, and HO•) generated in biological systems. Recently, several investigators have measured the second-order rate constants k_s for H atom abstraction by active free radicals from α-, β-, γ-, and δ-tocopherols in homogeneous solution, by using different experimental methods such as O_2 consumption,[1-3] ESR,[4] and stopped-flow spectrophotometry.[5] It was observed that the second-order rate constants, k_s, of tocopherols decrease in the order of $\alpha > \beta \sim \gamma > \delta$-tocopherol; further, the relative magnitudes of k_s, that is, the relative antioxidant activity of α-, β-, γ-, and δ-tocopherols, obtained from three different experimental methods agree well with each other.[5]

In order to obtain the tocopherol compounds having higher antioxidant activity than α-tocopherol and in order to clarify the structure–activity relationship in antioxidant action of tocopherols, several investigators, including the present authors, have prepared many tocopherol compounds.[2,3,6-15] It was found that a few tocopherols have

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