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The Synthesis of 1,2,3,4-Tetramethyl-5-nitronaphthalene and 1,2,3,4-Tetramethyl-6-nitronaphthalene

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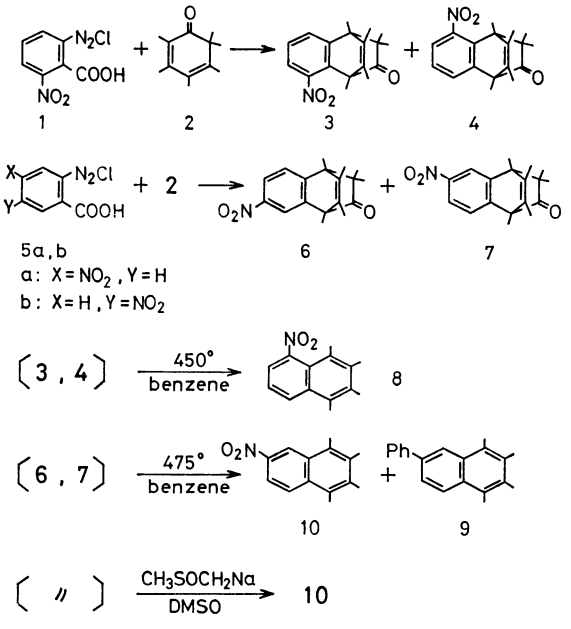
Synopsis. 1,2,3,4-Tetramethyl-5-nitronaphthalene and 1,2,3,4-tetramethyl-6-nitronaphthalene were prepared by the pyrolysis of 5- and 8-nitro-1,2,3,4,10,10-hexamethyl-1,4-dihydro-1,4-ethanonaphthalen-9-ones and their 6- and 7-nitro-isomers respectively.

Polymethyl-substituted nitronaphthalenes, in which one aromatic ring is fully substituted by four methyl groups and the other ring by a certain number of nitro groups, are of particular interest from the point of view of their electronic structures. Their syntheses, however, have not hitherto reported except in the cases of such homologues as dimethylnitronaphthalenes,[1] because a) the substitution on the α-position of naphthalenes by a bulky group, which causes a severe nonbonded peri-interaction, is difficult and b) the electrophilic nitration of polymethylnaphthalenes usually occurs on the methylated ring and often leads to abnormal reactions that take place on alkyl side chains.[2]

In this report, we wish to present the first syntheses of two tetramethylnitronaphthalenes, *i.e.*, 1,2,3,4-tetramethyl-5-nitro-naphthalene (**8**) and 1,2,3,4-tetramethyl-6-nitronaphthalene (**10**), prepared by a method that does not require the direct introduction of a nitro group on the naphthalene ring. This method is based on a modification of the one that has been used successfully to synthesize a number of polymethylnaphthalenes.[3] The synthetic process is outlined in Scheme 1.

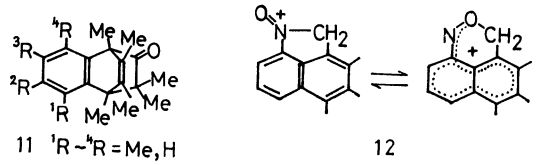
A mixture of Compound **6** and **7**, both of which were obtained from either 4- or 5-nitroanthranilic acid and hexamethyl-2,4-cyclohexadien-1-one (**2**),[4] was used as the precursor of naphthalene **10**, and it was subjected to the following two treatments: A) treatment with the methylsulfinylmethanide anion in dimethyl sulfoxide, and B) pyrolysis. Method A has been known to be an efficient method[3] to prepare a certain number of polymethylnaphthalenes from the methylaryne-adducts of Type **11**. By applying this method to the nitrobenzyne adducts (**6** and **7**) under various conditions, however, only a slight amount of **10** was formed (3%). Thus, Method A was found to be preparatively inadequate. (The same inapplicability was also encountered in the cases of chloro- and dichlorobenzyne-adducts.)



Scheme 1.

On the other hand, Method B proved effective. The pyrolysis of the adduct was carried out by means of a simple pyrolysis apparatus heated at 475±5 °C; it gave naphthalene, **10**, in a 60% yield. This naphthalene is thermally unstable, for the VPC analysis at 250 °C did not give any reliable chromatogram of **10**. Related to this characteristic, when the pyrolysis was carried out at 500 °C and above, 1,2,3,4-tetramethyl-6-phenylnaphthalene (**9**) was formed as the major by-product (>7%). It was apparently formed by the homolysis of **10** in the atmosphere of benzene.[5]

Similarly, nitronaphthalene **8** was obtained (16%) from a mixture of Compounds **3** and **4** by the pyrolysis at 450±5 °C. This nitronaphthalene **8** is also thermally unstable, and its VPC analysis was unsuccessful. Of particular interest is the fact that the mass spectrum of **8** taken while varying the chamber voltage between 80—12 eV showed its major fragment peak at *m/e* 212 (M^+-17). This is fragmentation behavior characteristic of **8**, differentiating it from **10**, and it can be interpreted in terms of the elimination of OH[6] from the peri-position (see **12**), where the 4-methyl and 5-nitro groups are subjected to a severe peri-interaction. This interaction is also illustrated by the ^{1}H-NMR spectra of **8**, in which the 4-methyl proton absorbs at a higher field (δ 2.31) than does the 1-methyl proton (2.61), indicating that the 5-nitro group is twisted perpendicularly to the ring plane.[7]



Experimental

Preparation of Nitrobenzyne-adducts ***3***, ***4***, ***6***, *and* ***7***. These compounds were prepared from the corresponding nitrobenzenediazonium-2-carboxylate hydrochlorides[8,9] by means of the reaction with hexamethyl-2,4-cyclohexadien-1-one (**2**)

according to the procedure previously reported.[4]

Pyrolysis Procedure. A vertically held Pyrex tube (15 mm ID × 300 mm length) packed with glass beads (5.5 mm OD) was heated at 450—500 °C under a gentle stream of nitrogen (15 ml/min). A benzene solution of the adduct mixture (6.0 g, 0.02 mol) in 120 ml of benzene was then dropped into this tube from the dropping funnel placed on the top of the tube. The pyrolyzed products were collected through a condenser that was connected to the bottom-end of the tube, and were chromatographed through a silica gel column (developing solvent: cyclohexane for **9**, cyclohexane/benzene=3 for **8**, and benzene for **10**) to give the nitronaphthalenes.

*1,2,3,4-Tetramethyl-6-nitronaphthalene (**10**).* The best yield of this naphthalene was attained by the pyrolysis performed at 475±5 °C; 60%. Mp 155—156 °C (recrystallized from cyclohexane, yellow needles); MS(*m/e*) 229 (M^+); ^{1}H-NMR(δ, CCl_4) 2.59 (6H, bs, α-Me), 2.42 (6H, bs, β-Me), 7.89—8.02 (2H, m, Ar-H at 7- and 8-positions), 8.74 (H, a pair of d, Ar-H at the 5-position); ^{13}C-NMR (δ, $CDCl_3$) Ar-Me at 15.3 (2Me), 17.4, and 17.7, Ar-C at 117.2, 120.8, 125.4, 129.1, 130.9, 133.7, 135.4, 137.8, and 143.9 (C-NO_2); UV(EtOH) max 222(ε 4.3×10^4), 280(2.9×10^4), and 326(8.7×10^3). Found: C, 73.26; H, 6.63; N, 6.21%. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.60; N, 6.11%.

When the pyrolysis was carried out at 500 ± 5 °C, 1,2,3,4-tetramethyl-6-phenylnaphthalene (**9**) was isolated from the chromatograph fraction that eluted faster than **10**. Yield, 8%; mp 135—136 °C(pet. ether); MS(*m/e*) 260 (M^+); ^{1}H-NMR(δ, CCl_4) 2.37 (6H, s, β-Me), 2.57 (3H, s, α-Me), 2.61 (3H, s, α-Me), 7.17—8.17 (8H, m, Ar-H); UV(EtOH) max 218 (ε 2.9×10^4), 260 (5.6×10^4), and 300 nm (8.8×10^3). Found: C, 91.99; H, 7.73%. Calcd for $C_{20}H_{20}$: C, 92.30; H, 7.69%.

*1,2,3,4-Tetramethyl-5-nitronaphthalene (**8**).* This naphthalene **8** was obtained in a 16% yield when the pyrolysis was performed at 450±5 °C. Mp 111—113 °C (recrystallized from cyclohexane, orange-yellow needles); MS(*m/e*) 229(M^+), 212(M^+-17, base peak); ^{1}H-NMR(δ, CCl_4) 2.31 (3H, s, 4-Me), 2.41 (6H, bs, 2- and 3-Me), 2.61 (3H, s, 1-Me), 7.17—7.68 (2H, m, Ar-H at 7- and 6-positions), 8.12 (H, a pair of d, J_1=8.2, J_2=1.6 Hz, Ar-H at 8-position); ^{13}C-NMR(δ, $CDCl_3$) Ar-Me at 15.8, 17.5, 17.7, and 18.1, Ar-C at 122.0, 122.4, 123.7, 127.0, 128.8, 129.3, 133.0, 135.2, 138.1, and 149.1 (C-NO_2); UV(cyclohexane) max 233(ε 4.2×10^4) and 260 nm (1.0×10^4). Found: C, 73.41; H, 6.57; N, 6.18%. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.60; N, 6.11%.

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6) A similar fragmentation pattern has been reported in the case of *o*-nitrotoluene, see J. H. Beynon, R. A. Saunders, A. Topham, and A. E. Williams, *J. Chem. Soc.*, **1965**, 6403; S. Meyerson, I. Puskas, and E. K. Fields, *J. Am. Chem. Soc.*, **88**, 4974 (1966).

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8) Caution should be taken when handling dry nitrobenzenediazonium-2-carboxylates, because they detonate upon heating or hammering. Their hydrochlorides, **1** and **5** can, however, be handled more safely.

9) 3-Nitroanthranilic acid was inadequate as a precursor of nitrobenzyne, because it undergoes the *ipso* substitution of the nitro group during the diazotization.