Nitration of 9,10-Dimethylanthracene and 9,10-Diethylanthracene[1]

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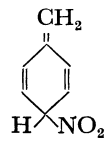
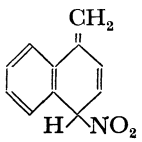
9,10-Dimethylanthracene gave 9-nitromethyl-10-methylanthracene as a major product, when treated with fuming nitric acid in dichloromethane at low temperatures. In contrast, 9,10-diethylanthracene yielded 9-nitro-10-hydroxy-9,10-diethyl-9,10-dihydroanthracene, which in refluxing alcohol was readily converted into 9,10-dialkoxy-9,10-diethyl-9,10-dihydroanthracene. Possible reaction sequences for the side-chain nitration have been discussed.

The mechanistic course of side-chain nitration of polymethylated aromatics proceeds along one of two paths depending on the nature of the substrate involved. Action of nitric acid upon polymethylbenzenes at low temperatures usually leads to the formation of benzyl nitrates.[2] In contrast, a similar treatment of polymethylnaphthalenes results in side-chain nitration, giving 1-naphthylnitromethanes as a major porduct.[3] Formation of these unusual products has been explained in terms of a nitromethylene cyclohexadiene intermediate (I or II), derived from the nitroarenium ion by proton release from the activated alkyl side-chain.[4] Thus, a marked difference in the modes of reaction observed for the benzene and the naphthalene series of compounds would be attributed to the presence of a fused benzene ring in the latter systems. If the dichotomy between the reaction courses taken in the nitration of benzenes on the one hand and of naphthalenes on the other comes from the difference in the relative stabilities of I and II, 9,10-dimethylanthracene (III) is expected to behave in a manner analogous to polymethylnaphthalenes, giving a side-chain nitrated product (VI), since the initial attack of nitronium ion on the hydrocarbon occurs at 9-position to form the arenium ion (IV), from which a nitromethylene cyclohexadiene (V) flanked with fused benzene rings on both sides would be formed (Scheme 1). The relative stability of the intermediate dienes should increase in the order I<II<V with an increase in the number of intact benzene rings. 9,10-Dimethyl- and 9,10-diethylanthracenes (III and IX) were prepared, their behavior towards the nitrating agent being investigated.



I

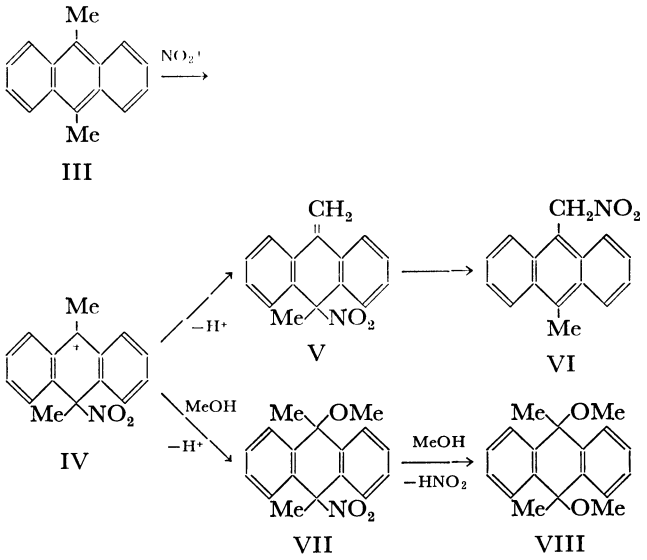


II

A dilute solution of III in purified dichloromethane was treated with two equivalent amounts of nitric acid (d=1.5) at −10——5 °C in the dark. Chromatography of the crude product on deactivated alumina gave rise to the isolation of a new crystalline compound (VI), mp 197—198 °C, as the main product (82%); molecular formula $C_{16}H_{13}NO_2$, infrared bands (NO_2) at 1546 and 1360 cm^{-1}, and proton resonances at δ 3.20 (s, 3H), 6.51 (s, 2H), 7.50—7.75 (m, 4H), and 8.23—8.55 (m, 4H). The mass spectrum showed the expected peaks at m/e 251 (M^+) and 205 (M^+–NO_2). The results are in line with its formulation as 9-nitromethyl-10-methylanthracene (VI). Its identity was further confirmed by an independent synthesis; 9-methylanthracene was chloromethylated to 9-chloromethyl-10-methylanthracene,[5] which was then treated with silver nitrite in acetonitrile to yield VI.

When III was treated with the nitrating agent in commercial dichloromethane of GR grade and the crude product mixture was passed over a deactivated alumina column, an appreciable amount of another nitro-compound (VII), with a composition fitting $C_{17}H_{17}NO_3$ best, was obtained besides VI. Proton NMR spectrum showed peaks at δ 1.64 (s, 3H), 2.16 (s, 3H), 2.91 (s, 3H), and 7.26—7.91 ppm (m, 8H). A molecular ion peak at m/e 283 is in line with the hypothesis that one more carbon atom is added to anthracene during the reaction. Additional peaks were observed at m/e 268 (M^+–Me), 253 (M^+–2Me), 237 (M^+–Me–MeO or M^+–NO_2), 222 (M^+–Me–NO_2), and 206 (M^+–MeO–NO_2). In the infrared spectrum, there were strong bands at 1535 and 1348 cm^{-1} (NO_2), and 1100 cm^{-1} (C–O–C). Heating of VII in methanol caused facile replacement of the nitro group by the methoxy group, giving a compound (VIII) with composition $C_{18}H_{20}O_2$. Proton NMR spectrum of VIII showed resonance at δ 1.63 (s, 6H), 2.80 (s, 6H), and 7.28—7.79 ppm (m, 8H) with an intensity ratio 3 : 3 : 4. Its mass spectrum showed peaks at 268 (M^+), 253 (M^+—Me), 237 (M^+—MeO), 222 (M^+—Me—MeO), and 206 (M^+—2MeO), its infrared spectrum indicating the presence of ether linkage (1100 cm^{-1}). Chemical and spectral data of VII and VIII are in line with the formulation of the former compound as 9-nitro-10-methoxy-9,10-dimethyl-9,10-dihydroanthracene and the latter as 9,10-dimethoxy-9,10-dimethyl-9,10-dihydroanthracene. *cis*-Configuration can be assigned to VIII by comparison with known spectral data.[6] Discrepancy in the results from the reactions in commercial dichloromethane and purified dichloromethane would be attributed to the presence of a very minor amount of methanol as an impurity or an antioxidant. A possible course for the formation is indicated in Scheme 1.

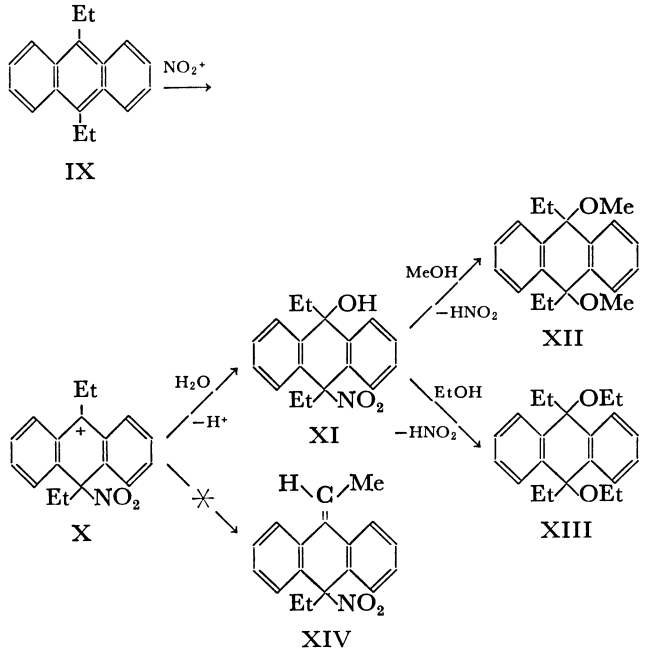
It is assumed that nitronium ion attacks hydrocarbon III to form arenium ion IV, which will release a proton from the activated methyl group at 10-position to form a methylene cyclohexadiene V, which is then transformed into nitromethyl compound VI. In the presence of methanol, the arenium ion IV would scavenge the nucleophile to form an addition product



Scheme 1.

VII rather than to release proton from the side-chain to form V.

When 9,10-diethylanthracene (IX) was allowed to react with nitric acid in purified dichloromethane, a single crystalline product with the composition $C_{18}H_{19}NO_3$ was isolated in a 47% yield. It showed infrared bands at 3540 (OH), 1542, and 1358 cm^{-1} (NO_2), and ^1H NMR peaks at δ 0.31 (t, 3H), 0.50 (t, 3H), 2.11 (q, 2H), 2.34 (s, H), 2.89 (q, 2H), and 7.30—8.01 ppm (m, 8H). The results are in line with the structure, 9-nitro-10-hydroxy-9,10-diethyl-9,10-dihydroanthracene (XI). When refluxed in methanol, XI was converted into a mixture of *cis*- and *trans*-9,10-dimethoxy-9,10-diethyl-9,10-dihydroanthracenes (XII), the former being predominant on prolonged heating.[6] A similar treatment of XI in ethanol led to the formation of 9,10-diethoxy-9,10-diethyl-9,10-dihydroanthracene (XIII).



Scheme 2.

Nitration of IX is in contrast to that of pentaethylbenzene, which gave 2,3,4,5-tetraethyl-α-methylbenzyl nitrate as the sole significant product.[7] Failure of IX to undergo reactions on the side-chain might be taken as an evidence for the intermediacy of a nitromethylene cyclohexadiene V in the side-chain substitution. Conversion of the arenium ion (X) into the diene (XIV) forces the ethylidene group to be coplanar with the *peri*-hydrogen atoms subjected to a considerable steric interaction. Thus, X would take up an anion to form an adduct XI rather than to release α-proton to form XIV (Scheme 2).

A sharp change in the modes of reaction towards the nitrating agent on passing from benzenes to naphthalenes and anthracenes would reflect the diminished tendency of the intermediate dienes II and V toward aromatization. With less stable diene I derived from polymethylated benzene, the initial process could involve heterolytic scission of the carbon-nitrogen bond to give a benzyl cation-nitrite ion pair. The benzylic cation carries most of its positive charge on the *exo*-cyclic carbon atom. Thus, it tends to recombine with the ambident nitrite ion at benzylic carbon atom through the more negative oxygen atom, giving benzyl nitrite which will be oxidized to the corresponding nitrate. With the more stable dienes II and V derived from polymethylated naphthalene and anthracene, their tendency to aromatize decreases due to the presence of one or two intact benzene nuclei. This corresponds to the partial formation of a positive charge on the *exo*-cyclic carbon atom, when the fission of the nitrogen-carbon bond takes place.[8] Thus, the combination of 1-naphthylmethylium and 9-anthrylmethylium ions with the ambident nitrite ion would occur preferably through the less negative nitrogen atom rather than oxygen atom, leading to the formation of side-chain nitro compounds.

Alternative explanations can be given for the conversion of nitromethylene cyclohexadienes into side-chain substitution products. The side-chain nitration might proceed via S_E2' mechanism which involves the attack of nitronium ion on the terminal methylene carbon of II or V, redistribution of electrons to regain the aromatic system, and the concomitant departure of the nitro group from the ring. The side-chain nitrooxylation might take place through a formally reversed sequence, S_N2' mechanism, which involves attachment of the nitrate ion to the terminal methylene carbon of I, departure of the nitro group as an anion, and reorganization of the system to aromatic nucleus.

Experimental

All melting points are uncorrected. Infrared spectra were measured in Nujol mulls with a Jasco DS-402G spectrophotometer. Proton NMR spectra were obtained for deuteriochloroform solutions on a Varian T-60 spectrometer with TMS as an internal standard.

9,10-Dimethylanthracene (mp 180—181 °C;[9] ^1H NMR: δ 3.07(s, 6H), 7.36—7.71 (m, 4H), and 8.20—8.55 ppm (m, 4H)) was prepared by the LAH reduction of 9,10-bis(chloromethyl)-anthracene,[10] and 9,10-diethylanthracene (mp 144—145

°C;[11] ^{1}H NMR: δ 1.39 (t, 6H), 3.49 (q, 4H), 7.41—7.78 (m, 4H), and 8.28—8.63 ppm (m, 4H)) was obtained by the reduction of 9,10-diethyl-9,10-dihydroxy-9,10-dihydroanthracene with stannous chloride in methanol.[12]

Purification of Dichloromethane Used as Solvent for Nitration. Commercial dichloromethane (GR grade as well as for spectroscopic use, Tokyo Kasei, Nakarai, Wako, and Katayama) was shaken several times with one-fifth its volume of concentrated sulfuric acid and then thoroughly washed with water. This was then shaken with 5%-aqueous sodium hydroxide, washed thoroughly with water, refluxed over calcium hydride for two hours, and finally distilled through an efficient column; the first and last portions of the distillate were discarded.

9-Nitromethyl-10-methylanthracene (VI). A warm solution of 9-chloromethyl-10-methylanthracene[5] (1.14 g) in acetonitrile (10 ml) was added all at once to a magnetically stirred solution of silver nitrite (1.0 g) in acetonitrile (5 ml). The mixture was stirred overnight and silver chloride was removed by filtration. The residue obtained after removal of the solvent was taken up in hot ethanol, from which VI separated as fine needles. Mp 196—198 °C. Yield, 0.5 g.

Found: C, 76.23; H, 5.25; N, 5.51%. Calcd for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22; N, 5.57%.

Procedure for the Nitration of 9,10-Dialkylanthracenes. 1) A solution of 9,10-dialkylanthracene (0.002 mol; 0.41 g for III and 0.47 g for IX) in purified dichloromethane (5 ml) was vigorously stirred with external cooling at −12 to −2 °C, and a solution of nitric acid (d=1.5; 0.002 mol, 0.86 ml) in the same solvent (4 ml) was added through a syringe over a period of 30 min. The mixture was kept in the dark at −10 to −5 °C for 3 hr and then quenched by the addition of water. The organic layer was separated, washed with dilute aqueous sodium hydrogen carbonate, and dried over anhydrous magnesium sulfate. The crystalline solid obtained after removal of the solvent was examined by infrared and proton NMR spectroscopy as well as by thin-layer chromatography.

Crude product (0.50 g) from III was crystallized from benzene to give VI as slightly yellow needles, mp 197—198 °C. Yield, 0.41 g (82%).

Found: C, 76.53; H, 5.27; N, 5.25%. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57%.

Crude product (0.59 g) from IX was recrystallized from a mixture of carbon tetrachloride and light petroleum to give XI as ivory-colored needles, mp 138—139 °C. Yield, 0.27 g (46%).

Found: C, 72.44; H, 6.40; N, 4.42%. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71%.

2) A solution of III (2.06 g, 0.01 mol) in dichloromethane (GR grade, 100 ml) was treated with nitric acid (d=1.5, 0.43 ml; 0.02 mol) in a similar manner to that for 1). A crude product (2.14 g) obtained after ordinary work-up was found to be a mixture of several compounds, as shown by a complicated feature of its proton NMR spectrum; at least eight prominent peaks were observed in the aromatic and aliphatic methyl proton regions (δ 1.64, 1.69, 1.78, 2.16, 2.36, 2.84, 2.91, and 3.20 ppm). Chromatography of this mixture on alumina gave VII from benzene eluates as needles, mp 152—155 °C. Yield, 0.75 g.

Found: C, 71.73; H, 5.99; N, 4.73%. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94%.

Alcoholysis of Addition Products. The addition product was dissolved in excess alcohol and heated under reflux for a few minutes. Evaporation of the solution gave the corresponding bis-alkoxy ether in a good yield.

VIII (*cis*): mp 161—166 °C.

Found: C, 80.34; H, 7.51%. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%.

XII (*cis*): mp 147—149 °C. ^{1}H NMR: δ 0.76 (t, 3H), 2.02 (q, 2H), 2.71 (s, 3H), and 7.23—7.78 ppm (m, 8H).[6,13] *trans*-Isomer exhibited absorptions at δ 0.27 (t, 3H), 2.08 (q, 2H), 2.90 (s, 3H), and 7.23—7.78 ppm (m, 8H).

XIII: mp 125—126 °C. ^{1}H NMR: δ 0.26 (t, 3H), 1.10 (t, 3H), 2.11 (q, 2H), 3.02 (q, 2H), and 7.20—7.80 ppm (m, 8H).

Found: C, 81.15; H, 8.75%. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70%.

The presence of only one set of signals in the proton NMR spectrum of XIII suggests that the obtained compound is one of the two possible geometrical isomers, probably *cis*, and not their mixture.

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