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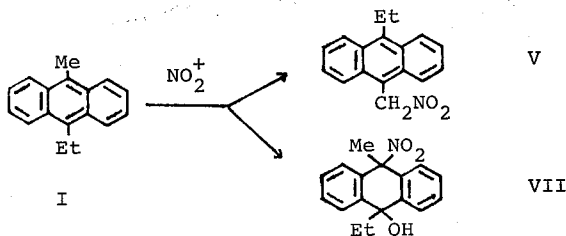
Nitration of 9-Ethyl-10-methylantracene, 9-Ethylantracene, and 9-Methylantracene¹⁾

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9, 10-Dimethylantracene and 9, 10-diethylantracene behave quite differently towards the action of nitric acid; the former compound has been shown to undergo side-chain nitration to give a nitromethyl derivative, while the latter gives rise to an addition product.²⁾ In order to confirm the strikingly different behavior of the methyl group as compared to the ethyl group towards nitrating agent, we have extended the investigation to include three additional 9-alkylantracenes.

Reaction of 9-ethyl-10-methylantracene (I) with an equivalent amount of nitric acid ($d=1.5$) in dichloromethane at -20 to -15°C gave a comparable mixture of two nitro compounds in good yield.



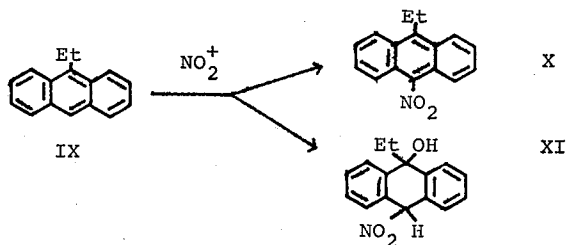
The molar proportion of nitric acid could be varied from one to two without any significant effect on the composition of the product. Column chromatography of the product mixture over alumina gave fine yellow crystals, mp $185\text{--}187^{\circ}\text{C}$. Elemental analysis and the molecular ion peak at m/e 265 in its mass spectrum proved its molecular formula as $\text{C}_{17}\text{H}_{15}\text{NO}_2$. Its infrared spectrum showed absorption bands at 1551 , 1301 , 796 , and 752 cm^{-1} , and the PMR spectrum showed peaks at δ 1.43, 3.63, 6.45, 7.44–7.84, and 8.21–8.59 ppm with relative areas 3:2:2:4:4. These data are in line with the structure, 9-ethyl-10-nitromethylantracene (V). Confirmation of the assigned structure was provided by the independent synthesis of V from 9-ethyl-10-chloromethylantracene and silver nitrite.

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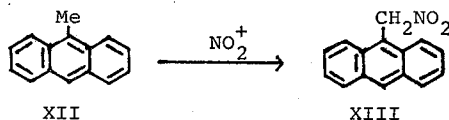
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Another nitro compound could not be obtained in pure form because of its gradual decomposition during work-up and chromatographic treatment. However, its structure could be deduced to be 9-ethyl-9-hydroxy-10-methyl-10-nitro-9, 10-dihydroanthracene (VII) on the basis of its spectral evidences. Infrared spectrum showed the presence of hydroxyl group (3540 cm^{-1}) and aliphatic nitro group (1545 and 1350 cm^{-1}). The PMR spectrum exhibited the presence of one methyl group, one ethyl group, and eight aromatic protons. A triplet at δ 0.57 and a quartet at δ 2.15 ppm could reasonably be attributed to a geminal ethyl-hydroxyl grouping. A geminal methyl-nitro grouping and eight side ring protons were indicated by a singlet at δ 2.30 and a multiplet at δ 7.4–8.6 ppm, respectively. The alternative structure (VIII) should give rise absorptions due to ethyl and methyl groups at around 0.5–0.6 (t), 1.5–1.7 (s), and 2.7–2.9 ppm (q), respectively.²⁾

A similar treatment of 9-ethylanthracene (IX) with nitric acid gave a crystalline solid, from which two nitro compounds were separated by fractional crystallization and chromatography. Their analyses and spectral data were consistent with structures 9-ethyl-10-nitroanthracene (X) and 9-ethyl-9-hydroxy-10-nitro-9, 10-dihydroanthracene (XI), respectively, as expected from ordinary modes of addition and substitution reactions. No product resulting from the attack on the ethyl group could be obtained. Extension of reaction time appeared to favor the formation of X at the expense of XI.

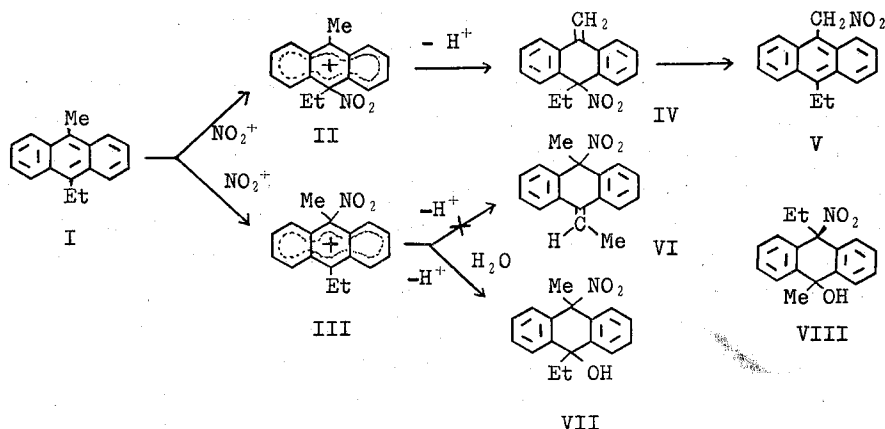


In contrast, a facile side-chain nitration occurred with 9-methylanthracene (XII), giving 9-nitromethylanthracene (XIII) in nearly quantitative yield.



The above results clearly indicate that methyl group is more reactive towards the nitrating agent than ethyl group.³⁾ This can reasonably be explained by the mechanism which we have suggested for the electrophilic side-chain substitution.^{2,4)} Nitronium ion attaches to the *meso* position of I to form two ions, viz., the methyl-stabilized ion (II) and the ethyl-stabilized ion (III). The former ion loses proton from the activated methyl group to form a nitromethylene cyclohexadiene (IV), which

is then converted to V. The latter ion III, not being energetically favored to form diene VI due to steric interaction between the methyl group and the *peri*-hydrogens of the anthracene nucleus, takes up nucleophile to form addition product VII (Scheme 1).



Scheme 1

EXPERIMENTAL

All mps were determined with a hot-stage apparatus and are uncorrected. Infrared spectra were measured in Nujol mulls with a Hitachi 215 spectrophotometer. PMR spectra were obtained with a Varian T-60 spectrometer in deuteriochloroform solutions containing TMS as internal standard.

9-Methylantracene (XII; mp 79–80°C)⁵ and 9-ethylantracene (IX; mp 54–56°C)⁵ were prepared by the reaction of anthrone and the corresponding alkylmagnesium bromides. 9-Ethyl-10-methylantracene (I; mp 145–147°C)⁶ was obtained from 9-chloromethyl-10-ethylantracene (mp 155–170°C with decomposition) by reducing with lithium aluminum hydride in tetrahydrofuran. All compounds were purified by chromatography over alumina and checked by PMR.

Nitration of Alkylanthracenes. All reactions were carried out in approximately the same manner as described previously.^{2,4}

1) Reaction of 9-Ethyl-10-methylantracene (I). PMR pattern of the yellow solid product contained resonances of two types of ethyl group and a singlet peak due to nitromethyl group, suggesting the presence of a side-chain substitution product and an addition product. The intensity ratio of the methylene resonance at δ 6.45 to the methyl proton resonances at δ 0.57 ppm was *ca.* 2:3, indicating the presence of two products in an approximate ratio 1:1. The mixture was subjected to column chromatography on alumina. Elution of the column with light petroleum (bp 40–60°C) containing 10% ether gave V as yellow fine needles, which was found to be identical with the authentic specimen.

V: mp 185–187°C.

Found: C, 76.80; H, 5.68; N, 5.21%. Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_2$: C, 76.96; H, 5.70; N, 5.28%.

Repeated extraction of the solid product with cold light petroleum followed by

recrystallization of the insoluble part from a mixture of light petroleum and benzene gave VII, which gradually underwent decomposition and gave no definite melting point nor satisfactory analysis.

2) Reaction of 9-Ethylanthracene (IX). PMR spectrum showed the solid product to be a comparable mixture of a substitution product X and an addition product XI, which were separated by fractional crystallization from *n*-pentane/benzene and column chromatography. The relative yield of these products varied depending on the work-up procedures, presumably due to the partial conversion of XI to X.

X: mp 119–120°C. IR: 1552 and 1349 cm^{-1} (NO_2); PMR: δ 0.38 (t, 3H), 2.86 (q, 2H), and 7.41–7.98 ppm (m, 8H).

Found: C, 76.57; H, 5.23; N, 5.51%. Calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_2$: C, 76.48; H, 5.21; N, 5.57%.

XI: mp 151–152°C. IR: 3356 (OH), 1547 and 1347 cm^{-1} (NO_2); PMR: δ 0.87 (t, 3H), 1.94 (q, 2H), 6.58 (s, 1H), and 7.32–8.02 ppm (m, 8H).

Found: C, 71.28; H, 5.64; N, 5.15%. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_3$: C, 71.36; H, 5.61; N, 5.20%.

3) Reaction of 9-Methylanthracene (XII). XII reacted more rapidly with nitric acid than did I and IX. The reaction mixture was evaporated *in vacuo* to yield a solid residue, which was recrystallized from ethanol to give XIII as yellow, fine needles.

XIII: mp 179–182°C. IR: 1551 and 1342 cm^{-1} (NO_2); PMR: δ 6.48 (s, 2H) and 7.35–8.69 ppm (m, 9H).

Found: C, 75.24; H, 4.63; N, 5.80%. Calcd for $\text{C}_{15}\text{H}_{11}\text{NO}_2$: C, 75.94; H, 4.67; N, 5.90%.

ACKNOWLEDGMENTS

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- (3) The order of reactivity $\text{CH}_3 < \text{C}_2\text{H}_5$ is in marked contrast to that, $i\text{-C}_3\text{H}_7 < \text{C}_2\text{H}_5 < \text{CH}_3$, usually observed in the side-chain substitution under radical conditions. A parallel behavior in the side-chain sulfonation has been noted by Cerfontain and coworkers when 9-ethyl-10-methylanthracene is treated with one equivalent of SO_3 -dioxane complex in dioxane as solvent (personal communication; March, 1976).
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