Nitration of 9,10-Dialkylphenanthrenes. Side-chain Nitrooxylation in Competition with Side-chain Nitration[1]

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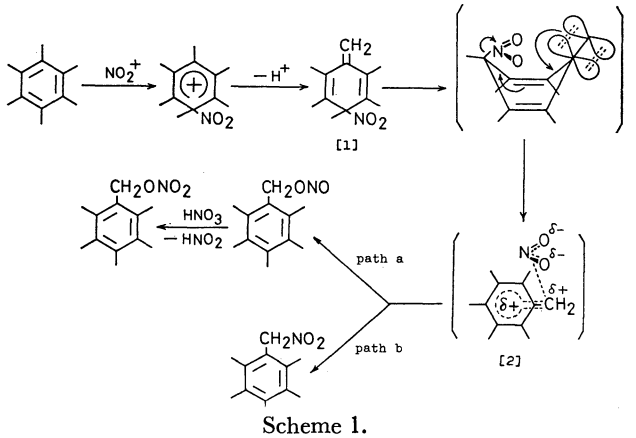
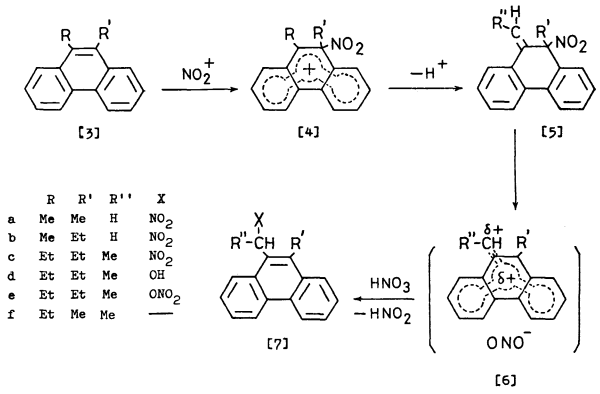
9,10-Dimethylphenanthrene and 9-methyl-10-ethylphenanthrene gave 9-methyl-10-nitromethylphenanthrene and 9-ethyl-10-nitromethylphenanthrene, respectively, as major product, when treated with fuming nitric acid in dichloromethane at low temperatures. In contrast, 9,10-diethylphenanthrene yielded a comparable mixture of products arising from side-chain nitration and side-chain nitrooxylation, which on chromatography over deactivated alumina gave 9-ethyl-10-(α-nitroethyl)phenanthrene and 9-ethyl-10-(α-hydroxyethyl)phenanthrene as main isolable products. 9-Methylphenanthrene and 9-ethylphenanthrene were both simply nitrated at the ring position to give the corresponding 9-alkyl-10-nitrophenanthrenes in good yields. No side-chain attack was observed. Factors responsible for determining which one of the competitive pathways will be followed have been discussed.

Reaction of polymethylbenzenes with fuming nitric acid often leads to the formation of products resulting from side-chain nitrooxylation (path a). In contrast, polymethylnaphthalenes and polymethylanthracenes can be attacked at the side-chain to yield naphthylnitromethanes and anthrylnitromethanes, respectively (path b). Both substitution processes have been suggested to involve nitromethylene cyclohexadiene intermediate with *para*-quinoid structure (**1**),[2] and a marked change in the modes of reaction towards the nitrating agent, observed on going from the benzenes to naphthalenes and anthracenes, has been related to the change in the development of carbonium ion character on the methylene carbon atom of intermediate ion pair (**2**) (Scheme 1).[3] In order to learn more about the mechanism of side-chain substitution and also to gain further insight into factors which determine whether path a or path b is followed, we have investigated the reaction of several alkylphenanthrenes with fuming nitric acid.



Scheme 1.

A dilute solution of 9,10-dimethylphenanthrene (**3a**) in purified dichloromethane was treated with an equivalent amount of nitric acid (d=1.5) at −10 °C and the dark brown mixture was allowed to stand in the refrigerator until the color had lightened. Quenching with water followed by chromatography of the crude product on deactivated alumina and recrystallization from chloroform–light petroleum resulted in the isolation of a new crystalline compound (**7a**), mp 175—176 °C, as principal product. **7a** had a molecular formula $C_{16}H_{13}NO_2$ and exhibited infrared bands due to nitro group at 1550 and 1361 cm^{-1}; proton NMR resonances at δ 2.81 (s, 3H), 6.09 (s, 2H), and 7.55—8.85 ppm (m, 8H). The mass spectrum showed the expected peaks at m/e 251 (M^+) and 205 (M^+-NO_2). These data are consistent with its formulation as 9-methyl-10-nitromethylphenanthrene (**7a**). This compound is unique in that it presents the first clear example of side-chain substitution which has occurred *via* nitromethylene cyclohexadiene with *ortho* quinoid structure (**5**). The overall reaction sequence is depicted in Scheme 2.



Scheme 2.

A similar reaction with 9-methyl-10-ethylphenanthrene (**3b**) yielded a yellow solid, the predominant component of which was readily separated by crystallization from ethanol and identified as 9-ethyl-10-nitromethylphenanthrene (**7b**) by its analysis and the usual spectroscopic measurements. Spectral inspection on a yellow syrupy residue from the mother liquor obtained in the recrystallization of the crude product indicated no appreciable formation of nitrate ester, which was not further sought for.

When 9,10-diethylphenanthrene (**3c**) was similarly allowed to react with nitric acid, a thick dark red liquid was obtained. It showed strong infrared bands at 1631—1635, 1278, and 860 cm^{-1}, indicating that the nitrate ester formation was a distinctly important process here. Proton NMR spectrum exhibited the characteristic

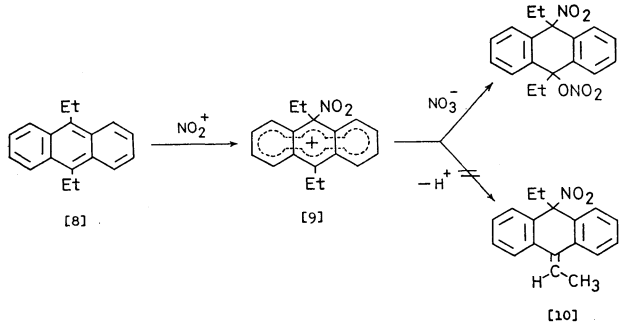
methyl and methylene splittings of two α-substituted ethyl groups, suggesting the presence of two major products arising from the attack in the α-position of ethyl groups. The signal integration revealed that these products were formed in almost equal amounts. When the product mixture was chromatographed over silica gel, slightly yellow needles melting at 107—110 °C was obtained from cyclohexane containing benzene eluates, and a low-melting glassy substance eluted from a mixture of benzene and methanol. The former compound with an elemental composition of $C_{18}H_{13}NO_2$ showed infrared bands for nitro group at 1548 cm^{-1}; proton NMR peaks due to ethyl group at 1.39 (t, 3H) and 3.23 (q, 2H), one methyl group at 2.16 (d, 3H), one methine proton at 6.33 (q, 1H), and aromatic protons at 7.36—8.89 ppm (m, 8H). On the basis of these evidences structure 9-ethyl-10-(α-nitroethyl)phenanthrene (**7c**) was assigned to the compound. The latter product with an approximate composition $C_{18}H_{18}O$ had the strong, broad infrared band due to hydroxyl group at 3540 cm^{-1}; proton NMR peaks at δ 1.38, 1.80, 3.26, 5.95, and *ca.* 7.5—9.2 ppm with the respective integrated peak area ratio of 3: 3: 2: 1: 8. These data support the assignment of structure 9-ethyl-10-(α-hydroxyethyl)phenanthrene (**7d**) to the product, characterization of which then allowed identification of a second major component in the original product mixture as 9-ethyl-10-(α-nitrooxymethyl)phenanthrene (**7e**). This would be the first case reported of the extensive nitrooxylation which occurs on an alkyl group of polycyclic aromatics and is contrasted with the reaction of 9,10-diethylanthracene (**8**) in which the only reaction that proceeds is the addition reaction.[3]

Under comparable conditions both 9-methylphenanthrene and 9-ethylphenanthrene were simply nitrated at the ring position and gave a good yield of 9-methyl-10-nitrophenanthrene and 9-ethyl-10-nitrophenanthrene, respectively. No side-chain attack was observed.

So far little work has been made of the nitration of alkyl derivatives of phenanthrene, but it is clear that 9- and 10-positions would maintain their reactivity.[4] Thus, nitronium ion attaches to the position carrying alkyl group to form arenium ion (**4**), which loses proton from the activated alkyl group on the adjacent carbon atom to give nitromethylene cyclohexadiene intermediate (**5**). **5** could collapse by heterolytic C–N bond fission to give a phenantrylmethylium-nitrite ion pair (**6**), the cationic component of which can dissipate its positive charge from the *exo*-cyclic carbon atom into two intact benzene nuclei. In a nitrite ion the the nitrogen atom has a much less electron density than oxygen atoms. A preferential bonding of 9-phenantrylmethylium ions (**6a** and **6b**) to the nitrogen atom of the ambident anion would then yield the observed nitro compound (**7a** and **7b**) (Scheme 2).

In contrast to **5a** and **5b**, diene **5c** affords a carbonium ion with branched structure (**6c**). This would mean the increase in the development of carbonium ion character in the cationic component of the ion pair **6c**. The greater the carbonium contribution, the greater would be the tendency for nitrite ion to form a covalent linkage at the atom having the higher electron density. Thus in recombining with the cationic center, oxygen atoms can effectively compete with the nitrogen atom, leading to the concurrent formation of nitro compound and nitrite ester. The latter compound is not stable in the presence of nitric acid and rapidly converted into the corresponding nitrate **7e**. The order of nitrate-forming tendencies as derived from the present work is **3c**≫**3b**>**3a**, which suggests that the mode of reaction is determined by the same factors that govern selectivity in the alkylation of the ambident anions.[5] The results are just what would have been predicted on the basis of the concept of "hard and soft acids and bases."[6]

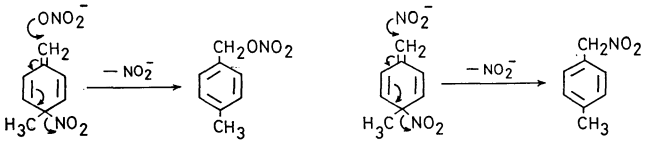
One may ask why the nitrate formation is prominent in the nitration of **3c**, but is not in the nitration of 9,10-diethylanthracene (**8**). The answer would appear to be related to a lesser degree of steric hindrance involved when arenium ion (**4**) comes in to form a nitromethylene cyclohexadiene **5c** than when ion **9** comes in to form diene **10**. Consequently, with **8** the addition product formation wins out over the side-chain substitution (Scheme 3).[3]



Scheme 3.

Spectral inspectrion of a product mixture from **3b** revealed that methyl group is much more reactive than ethyl group towards side-chain substitution. This result would be expected if one takes into account: 1) the greater contribution of intermediate ion **4b** relative to **4f** due to the partial relief of steric strain and the favorable inductive effect of ethyl group, 2) the relative ease of hyperconjugative proton release from the activated alkyl groups, and 3) the increase in steric interference with *peri*-hydrogen atom when the cyclohexadiene **5f** is formed.

An alternative possible route, which we have previously suggested for side-chain nitrooxylation of polymethylbenzenes[7] and could equally well explain the results, involves a nucleophilic attack of nitrate or nitrite anions at the *exo*-methylene group of **5** with simultaneous loss of the nitro group as nitrite anion (Scheme 4). The increase in nitrate-formation on going from **3a** to **3c** to polymethylbenzenes could con-



Scheme 4.

ceivably derive from difference in the proportion of S_N1' and S_N2' character in the transition state. Unfortunately, this pathway lacks good formal analogies in the literature as far as the authors are aware. In a recent paper,[8] some detailed discussion in favor of this mechanism has been made by Fischer and Ramsay in connection with their work on the adduct formation in the nitration of polymethylbenzenes. We do not feel, however, that sufficient data are yet available to be able to dismiss in a definite manner either of the two mechanisms proposed.

Experimental

All melting points are uncorrected. Infrared spectra were run in Nujol mulls on a Jasco DS-402G spectrophotometer. Proton NMR spectra were taken for deuteriochloroform solutions on a Varian T-60 spectrometer using TMS as internal standard. Mass spectra were obtained on a Hitachi RMS-4 spectrometer. Thin-layer chromatography on silica gel G was used for monitoring reactions and chromatographic separations. Indication was effected with iodine vapor or ultraviolet light.

9,10-Dialkylphenanthrenes were prepared by the reaction of 10-lithio derivatives of related 9-alkylphenanthrenes[9] with methyl and ethyl iodides, and purified by chromatography over alumina followed by recrystallization from benzene–light petroleum. Physical properties of some phenanthrene derivatives obtained in connection with the present work are summarized in Table 1. To our knowledge, compounds **7a** to **7e** are not previously described in the literature.

Dichloromethane used as solvent for the nitration was purified according to our procedure described in a previous paper of this series.[3] Yields are based on product isolation.

Procedure for the Nitration of 9,10-Dialkylphenanthrenes. 9,10-Dialkylphenanthrene (0.002 mol; 0.41 g for **3a**; 0.44 g for **3b**, and 0.47 g for **3c**) was dissolved in dichloromethane (5 ml) and vigorously stirred with external cooling at −10 °C. After slow addition of nitric acid (d=1.5; 0.002 mol, 0.86 ml) in the same solvent (5 ml) through a syringe over a period of 30 min, the mixture was kept in the dark at 0 °C for 2 hr and at room temperature for 30 min, 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 light yellow crystalline residue or syrupy liquid obtained after removal of the solvent was examined by infrared and proton NMR spectroscopy as well as thin-layer chromatography.

1) A crude product from **3a** was crystallized from a mixture of benzene and cyclohexane to give **7a** as faintly yellow needles, mp 175—176 °C. Yield, 0.43 g (86%).

Found: C, 76.57; H, 5.21; N, 5.53%. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57%.

2) A crude product from **3b** was crystallized from chloroform–pentane to give **7b** as white, fine needles, mp 172—174 °C. Yield, 0.34 g (64%). IR: 1548, 1328, 756, and 717 cm^{-1}; Mass: m/e 265 (M^+) and 219 (M^+-NO_2).

Found: C, 77.32; H, 5.84; N, 5.02%. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28%.

A syrupy residue obtained from the mother liquor showed infrared bands at 1632, 1276, and 853 cm^{-1}, indicating the presence of slight amounts of nitrate ester.

3) An oily product from **3c** failed to produce a solid on standing in refrigerator. It was then placed on a column of silica gel developed with cyclohexane. Elution with cyclohexane followed by a mixture of cyclohexane and benzene yielded unchanged hydrocarbon and **7c**. The latter recrystallized from benzene–chloroform appeared as slightly yellow needles, mp 107—110 °C. Mass: m/e 279 (M^+) and 233 (M^+-NO_2).

Found: C, 77.40; H, 6.07; N, 4.98%. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.14; N, 5.01%.

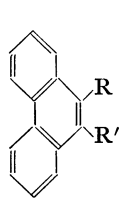
Further elution with benzene followed by 10%-methanol in benzene yielded a sticky glass, which we were unable to obtain in pure form but identified as **7d** by its NMR and IR spectra.

Found: C, 85.86; H, 7.15%. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25%.

Finally, elution of the column with methanol produced a trace of red-brown oil that was not further characterized.

Products from 9-methylphenanthrene and 9-ethylphenanthrene were recrystallized from a mixture of light petroleum and ether, and melted at 171—172 °C and 101—103 °C, respectively. Structural assignments were made on the basis of the analyses, NMR, and IR, spectra. Minor isomeric

Table 1. Physical properties of some 9,10-disubstituted phenanthrenes

Compound	R	R′	Mp (°C)	^{1}H NMR Spectra (δ)
	CH_3	CH_3	145—147[11]	2.73 (s, 6H), 7.35—7.78 (m, 4H), 7.97—8.29 (m, 2H), 8.56—8.89 (m, 2H)
	CH_3	C_2H_5	81—83[12]	1.27 (t, 3H), 2.70 (s, 3H), 3.30 (q, 2H), 7.53—9.05 (m, 8H)
	C_2H_5	C_2H_5	102—104[11]	1.38 (t, 6H), 3.27 (q, 4H), 7.48—8.92 (m, 8H)
	CH_3	CH_2NO_2	175—176	2.81 (s, 3H), 6.09 (s, 2H), 7.55—8.85 (m, 8H)
	C_2H_5	CH_2NO_2	172—174	1.38 (t, 3H), 3.19 (q, 2H), 6.12 (s, 2H), 7.50—8.94 (m, 8H)
	C_2H_5	$CH(CH_3)NO_2$	107—110	1.39 (t, 3H), 2.16 (d, 3H), 3.23 (q, 2H), 6.33 (q, 1H), 7.36—8.89 (m, 8H)
	C_2H_5	$CH(CH_3)OH$	—[a]	1.38 (t, 3H), 1.80 (d, 3H), 3.26 (q, 2H), 5.95 (q, 1H), 7.5—9.2 (m, 8H)

a) Glassy substance with no definite melting range.

products were not sought for.

9-Methyl-10-nitrophenanthrene:[10] IR: 1517 and 1228 cm^{-1}; ^1H NMR: δ 2.64 (s, 3H) and *ca.* 7.4—8.9 ppm (m, 8H).

Found: C, 75.83; H, 4.55; N, 5.96%. Calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90%.

9-Ethyl-10-nitrophenanthrene: IR: 1519 and 1368 cm^{-1}; ^1H NMR: δ 1.40 (t, 3H), 2.05 (q, 2H), and 7.51—8.87 ppm (m, 8H).

Found: C, 76.52; H, 5.20; N, 5.50%. Calcd for $C_{16}H_{15}NO_2$: C, 76.52; H, 5.21; N, 5.57%.

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