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Nitration of a Crude 9,10-Dihydrophenanthrene

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The preferred site of 9,10-dihydrophenanthrene (**1**) for typical S_AE reactions such as Friedel-Crafts acylation [1], nitration [2], sulphonation [3] and halogenation [4] is position 2, and these reactions are therefore the methods of choice for obtaining 2-substituted (or 2,7-disubstituted) derivatives of **1.** Since these derivatives are easily dehydrogenated, they are also useful for preparing 2-substituted (or 2,7-disubstituted) derivatives of phenanthrene [5], which generally cannot be obtained by direct substitution of phenanthrene itself.

In our laboratory, we have recently required considerable quantities of 2-nitro-9,10-dihydrophenanthrene (**2**) as the starting material for the preparation of 7-fluoro-9,10-dihydro-2-phenanthrylalkanoic acids [6]. To this end, we have developed a quick, easy method for obtaining multigram quantities of **1** by Birch reduction of phenanthrene [7]. However, the difficulty of purifying **1** from the crude product obtained (typically 91 % **1,** 3–4 % phenanthrene and 5–6 % polyhydrophenanthrenes) has led us to explore the possibility of obtaining quickly sufficient quantities of **2** by direct nitration of the crude product. We report our findings here.

Table 1 Conditions tried for nitration of 9,10-dihydrophenanthrene[a)]

Entry	Solvent/ Total volume (ml)	Reagent/ (mmol)	Temp. °C	Time[b)] (h)	**2** content[c)]
1	Ac_2O/60	HNO_3/78	5	24	32 %
2	AcOH/20	HNO_3/98	15	2	57 %
3	AcOH/20	HNO_3/98	5	6	71 %
4	CH_2Cl_2/1200	N_2O_4/44	25	4	30 %[d)]
5	CH_2Cl_2/36	$HNO_3 \cdot SnCl_4$/21	25	1	66 %

[a)] Crude product of the reduction of phenanthrene (4.0 g), 91 % **1** (20 mmol).

[b)] Longer reaction times did not increase the **2** content of the final crude mixture.

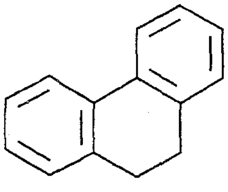
[c)] Percentage of the total amount of volatile components detected by g.l.c. (UCC, 200 °C) in the crude reaction product.

[d)] 6 % of unreacted **1** was also detected.

To optimize the yield of **2,** nitration was carried out under various experimental conditions with fuming nitric acid in acetic anhydride or glacial acetic acid. Other reagents that have been recommended for the nitration of polycyclic hydrocarbon or non-deactivated aromatic substrates, such as dinitrogen tetroxide [8], or the complex of fuming nitric acid with tin tetrachloride [9], were also tried. The most significant results are listed in Table 1. G.l.c. of the crude products showed that the major product, **2,** was in all cases accompanied by varying quantities of numerous by-products, and during purification of **2** up to 30 % of the crude product was also found to consist of non-volatile tars that had not been detected by g.l.c. All the nitrating agents and/or conditions produced roughly equal quantities of tar except N_2O_4, which produced more. For large scale preparation of **2** we chose the agent and conditions with the greatest degree of conversion of **1** into **2,** HNO_3 in glacial acetid acid (Table 1, entry 3).

Most tar was removed from the product by column chromatography on silica gel. Recrystallization and/or rechromatography of the fractions separated allowed the isolation of the major product, **2,** the known compounds 3-nitrophenanthrene (**3**) and 2,7-dinitro-9,10-dihydrophenanthrene (**4**), and two compounds of melting points 179–180 °C (**X**) and 84–85 °C (**Y**) for which we found no mention in the literature.

Microanalysis and m.s. of **X** indicated the molecular formula $C_{14}H_{10}N_2O_4$, and the chief m.s. fragments pointed to its being a dinitro-9,10-dihydrophenanthrene isomer of **4.** Its ^{1}H-n.m.r. spectrum had an AA'BB'-type symmetric multiplet centred at 2.94 ppm that is typical of asymmetrically substituted derivatives of **1,** such as **2** and others [6], when examined at 250 MHz (the spectra of symmetric derivatives such as **4** have a sharp singlet in this region). The chemical shifts and coupling constants of the other proton signals showed the nitro substituents to occupy positions 2 and 5, making **X** 2,5-dinitro-9,10-dihydrophenanthrene (**5**). The internal clustering of this molecule that is revealed by Dreiding models forces the nitro



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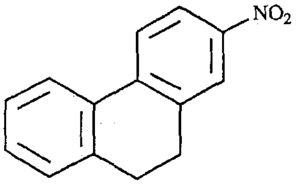

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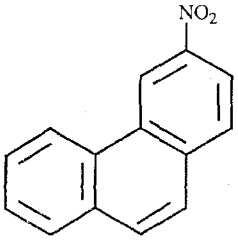

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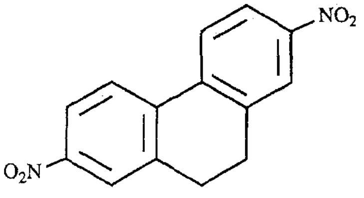

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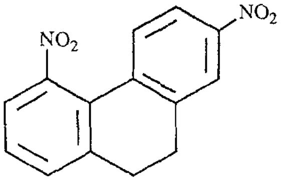

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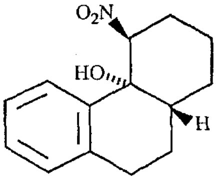

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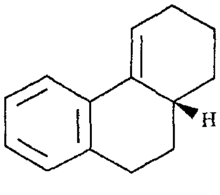

(7)

group in position 5 to lie out of the plane of its ring, so reducing conjugation between the two. This may be why this group has only a relatively small influence on the chemical shift of the proton *para* to it, 8-H. The anisotropic influence of this group must explain the shielding of 4-H (δ 7.41 ppm in **5** as against δ 7.87 ppm in **2**). Assignment of the nitro groups to any positions other than 2 and 5 would clearly contradict the observed n.m.r. spectrum.

Microanalysis and m.s. of **Y** yielded the molecular formula $C_{14}H_{17}NO_3$, and since its i.r. spectrum clearly reflected the presence of hydroxyl and nitro groups it must be a nitrooctahydrophenanthrenol. Surprisingly, its n.m.r. spectrum had signals for four protons in the δ 7.10–7.50 ppm region, so that the nitro group cannot be bound to the aromatic ring. The rest of the n.m.r. spectrum was too complex to allow a reliable structural assignment, but X-ray diffraction analysis[1] showed **Y** to be *rac*-(4R*,4aS*,10aS*)-4-nitro-1,2,3,4,4a,9,10,10a-octahydrophenanthren-4a-ol (**6**). Given this information, most of the n.m.r. signals can be identified satisfactorily.

The production of **4** and **5** during nitration of our crude **1** is readily explicable. **4** has been reported to be the chief product of the dinitration of **1** [5a], and **5** is probably the result of the nitration of 4-nitro-9,10-dihydrophenanthrene, the major by-product of the mononitration of **1** [2a,4c]. The presence of **3** is not surprising either, since the crude starting material contained a small proportion of phenanthrene. The most intriguing by-product, **6**, must derive from the addition of the components of nitric acid to one of the polyhydrophenanthrenes present in the starting material. The *trans*-diaxial location of its two functional groups on adjacent carbons suggests that it may come about through ionic addition of acetyl nitrate to 1,2,3,9,10,10a-hexahydrophenanthrene (**7**), followed by hydrolysis of the acetoxyl group during work-up in aqueous medium.

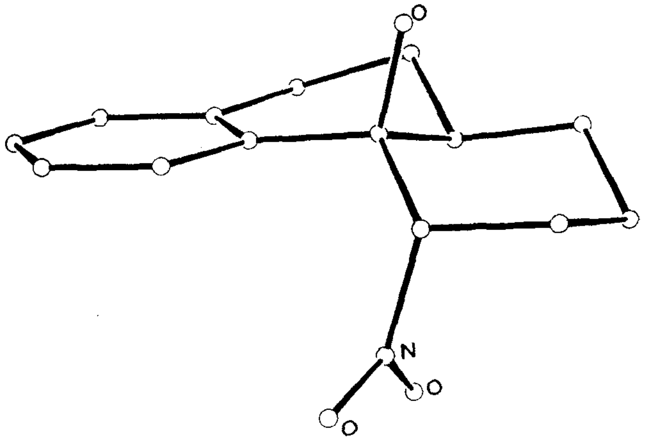

Fig. 1 Perspective view of the molecular structure of (**6**)

Experimental

Crude 9,10-dihydrophenanthrene was prepared by Birch reduction of phenanthrene [7], and was 91 % **1**, 3 % phenanthrene, and 6 % undetermined polyhydrophenanthrenes. Silica gel (230 mesh) was purchased from Merck. Other reagents and solvents were of commercial quality, purchased from Aldrich Chemical Co. N_2O_4 was prepared by thermal decomposition of anhydrous $Pb(NO_3)_2$, and was bubbled into a suitably sized sample of CH_2Cl_2. The amount of N_2O_4 was determined by differential weighing. Melting points were determined on a Kofler Thermopan Reichert apparatus and are uncorrected. Microanalyses were performed with a Perkin-Elmer 240B element analyser by the Microanalysis Service, University of Santiago, and were all within ± 0.25 % of the theoretical value. I.r. spectra were recorded on a Perkin-Elmer 681 spectrometer and ^{1}H-n.m.r. spectra on a Bruker WN 250 (250 MHz) spectrometer. M.s. were obtained with a Varian MAT-711 mass spectrometer at 70 eV. G.l.c. was carried out on a Hewlett Packard 5710A instrument equipped with an FID and an HP-3380S integrator. Columns, 10 % UCC on Chromosorb W AWDCS (50 cm × 1/8 ") at 200 °C or 10 % OV-101 on Chromosorb W-HP (2 m × 1/8 ") at 250 °C; carrier gas, N_2, 20 ml/min.

Nitration with fuming HNO_3 in acetic anhydride or acetic acid

Fuming nitric acid (d 1.5) was added very slowly with stirring to a solution of crude dihydrophenanthrene (4.0 g) in Ac_2O or

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[1] Partial or full data of the X-ray analysis can be obtained from one of us (G. Rodríguez).

AcOH kept at 0–5 °C. Once homogeneous, the reaction mixture was left for several hours at the temperatures listed in Table 1, and then poured onto crushed ice (200 g) and extracted with Et_2O (2 × 125 ml). The combined extracts were washed with 5 M NaOH (2 × 50 ml) and water (3 × 50 ml) and dried (Na_2SO_4). Removal of solvent under reduced pressure left a dark brown oily residue (5.03 g) that was analysed by g.l.c. (UCC). A sample of **2** was isolated from this crude product as described below.

Nitration with N_2O_4

To a solution of N_2O_4 (4.05 g, 44 mmol) in CH_2Cl_2 (400 ml) was added a solution of crude dihydrophenanthrene (4.0 g) in CH_2Cl_2 (800 ml), and the homogeneous mixture was left at room temperature for 4 h, after which the solvent and the excess reagent were evaporated off under reduced pressure to leave a residue (4.96 g) that was analysed by g.l.c. (UCC). A sample of **2** was isolated from this crude product by chromatography on silica gel (100 g) using CCl_4 (10 × 100 ml) as eluent. This purification procedure was not significantly better than that described below.

Nitration with the complex $HNO_3 \cdot SnCl_4$

The reagent was prepared by dissolving fuming HNO_3 (d 1.5; 1.1 ml, 21.5 mmol) and $SnCl_4$ (2.5 ml, 21.4 mmol) in CH_2Cl_2 (27 ml) at -5 °C. The resulting solution was added dropwise to a stirred solution of crude dihydrophenanthrene (4.0 g) in CH_2Cl_2 (9 ml), at 0 °C, and the mixture was left for 1 h at room temperature, and poured onto water (200 ml). The organic layer was drawn off, and the aqueous layer extracted with CH_2Cl_2 (2 × 100 ml). The combined organic extracts were washed with water (3 × 50 ml) and dried (Na_2SO_4), and the solvent was removed under reduced pressure. The residue was disintegrated in C_6H_6 (700 ml), and a green-grey inorganic precipitate was filtered out. The solvent was evaporated off from the clear filtrate to leave a dark oily residue (4.69 g) that was analysed by g.l.c. (UCC). A sample of **2** was isolated from this crude product by chromatography as described below.

Fractionation of the crude reaction product (preparative scale)

The pooled crude product of various runs performed in the best conditions (Table 1, Entry 3) (100 g) was loaded on a silica gel (2000 g) column and successively eluted with 1:1 heptane-C_6H_6 (12 l), C_6H_6 (6 l), 1:1 C_6H_6-Et_2O (6 l) and Et_2O (6 l). 1 l fractions were collected and analysed by g.l.c. (OV-101), and those of similar composition were pooled.

Fractions 4–6 left a solid residue (24.66 g) that was recrystallized twice from EtOH to yield **2** (15.01 g; purity > 99 % by G.L.C.). The residue obtained from the first mother liquor was recrystallized twice from EtOH and once from AcOH to afford **3** (0.11 g).

Fractions 10–12 left an oily residue (1.61 g) that was dissolved in Et_2O. This solution was left at room temperature to evaporate slowly from an open erlenmeyer flask, giving rise to a partially crystallized residue. Once isolated, the solid was recrystallized from AcOH to give **5** (0.08 g).

Fractions 13–14 left a solid residue (1.72 g) that was recrystallized once from EtOH and twice from AcOH to yield **4** (0.19 g).

The highly viscous oily residue of fractions 19–30 (those eluted with 1:1 C_6H_6-Et_2O and Et_2O; 41.29 g) was reloaded on a column of silica gel (900 g), successively eluted with C_6H_6 (7.5 l), 1:1 C_6H_6-Et_2O (1 l) and Et_2O (2 l), and collected in 500 ml fractions. The residue of fractions 16–21 (17.70 g) was composed largely of compounds that were highly polar and/or of high molecular weight, and that were not detected by g.l.c. under the conditions used (OV-101, 250 °C). The residue of fractions 9–10 (4.5 g) was rechromatographed (silica gel, 900 g; eluent 1:1 heptane-C_6H_6 (6 l); 200 ml fractions) and the fractions 5–14 from this last procedure left a viscous oily residue (1.39 g) which upon being left for 1 month in the refrigerator partially crystallized to afford a solid that was recrystallized from hexane to yield pure **6** (0.24 g).

2-Nitro-9,10-dihydrophenanthrene (**2**) had m.p. 82–83 °C (lit., 81–82 °C [2]). I.r. (KBr, cm^{-1}): 1590, 1510 (N=O), 1480, 1340 (N=O), 800, 780, 750; ^1H-n.m.r. ($CDCl_3$, δ ppm): 2.89–3.03 (m, 4H, -CH_2CH_2-), 7.28–7.40 (m, 3H, 6,7,8-H); 7.78–7.82 (m, 1H, 5-H), 7.87 (d, J 8.5 Hz, 1H, 4-H), 8.12 (d, J 2.3 Hz, 1H, 1-H), 8.16 (dd, J 8.5 and 2.3 Hz, 1H, 3-H).

3-Nitrophenanthrene (**3**) had m.p. 172–173 °C (lit., 172–174 °C [10]). I.r. (KBr, cm^{-1}): 1500 (N=O), 1340 (N=O), 1230, 890, 850, 760, 740; ^1H-n.m.r. ($CDCl_3$, δ ppm): 7.69–7.75 (m, 1H, 7-H), 7.76–7.82 (m, 1H, 6-H), 7.82 (A part of a AB system, J 9.0 Hz, 1H, 10-H), 7.96 (B part of a AB system, J 9.0 Hz, 1H, 9-H), 7.97 (virtual d, J 8.3 Hz, 1H, 8-H), 8.02 (d, J 8.8 Hz, 1H, 1-H), 8.40 (dd, J 8.8 and 2.1 Hz, 1H, 3-H), 8.77 (virtual d, J 8.1 Hz, 1H, 5-H), 9.62 (d, J 2.1 Hz, 1H, 4-H).

2,7-Dinitro-9,10-dihydrophenanthrene (**4**) had m.p. 227–228 °C (lit., 226 °C [5a]). I.r. (KBr, cm^{-1}): 1510 (N=O), 1345 (N=O), 1310, 910 830, 790, 740; ^1H-n.m.r. ($CDCl_3$, δ ppm): 3.05 (s, 4H, -CH_2CH_2-), 7.94 (d, J 8.5 Hz, 2H, 4,5-H), 8.18 (d, J 2.3 Hz, 2H, 1,8-H), 8.22 (dd, J 8.5 Hz and 2.3 Hz, 2H, 3,6-H).

2,5-Dinitro-9,10-dihydrophenanthrene (**5**) had m.p. 179–180 °C. I.r. (KBr, cm^{-1}): 1515 (N=O), 1345 (N=O), 895, 810, 800, 785, 735; ^1H-n.m.r. ($CDCl_3$, δ ppm): 2.86–3.02 (m, 4H, -CH_2CH_2-), 7.41 (d, J 8.7 Hz, 1H, 4-H), 7.43 (dd, J 7.8 and 7.2 Hz, 1H, 7-H), 7.52 (virtual d, J 7.2 Hz, 1H, 8-H), 7.63 (dd, J 7.8 and 1.2 Hz, 1H, 6-H), 8.05 (dd, J 8.7 and 2.4 Hz, 1H, 3-H), 8.17 (d, J 2.4 Hz, 1H, 1-H). MS (m/z): 270(M^+, 25 %), 223 (19), 196 (40), 195 (15), 194 (70), 193 (38), 178 (40), 177 (33), 176 (55), 168 (23), 167 (35), 166 (50), 165 (100), 152 (45).

(4R*, 4aS*,10aS*) - 4-Nitro -1,2,3,4,4a,9,10,10a - octahydrophenanthren-4a-ol (**6**) had m.p. 84–85 °C. I.r. (KBr, cm^{-1}): 3570 (O–H), 1535 (N=O), 1450, 1370 (N=O), 1300, 950, 935, 820, 785, 760, 720; ^1H-n.m.r. ($CDCl_3$, δ ppm): 1.59–1.74 (m, 5H, 1*eq*,2*eq*,2*ax*,10*eq*,10*ax*-H), 1.67 (s, exchang with D_2O, 1H, O-H), 1.85 (virtual qxd, J = 12.8 and 5.6 Hz, 1H, 1*ax*-H), 2.33 and 2.44 (AB system with J 16.3 Hz, each part additionally splitted as multiplets, 2H, 3*eq*,3*ax*-H), 2.53–2.65 (m, 1H, 10*aax*-H), 2.83 (A part of a AB system (J 17.3 Hz), additionally splitted as a dd, J 5.6 and 1.7 Hz, 1H, 9*ψeq*-H), 2.95 (B part of a AB system (J 17.3 Hz), additionally splitted as a dd, J 12.2 and 5.7 Hz, 1H, 9*ψax*-H), 5.41 (dd, J 4.7 and 2.5 Hz, 1H, 4*eq*-H), 7.12–7.15 (m, 1H, 5-H or 8-H), 7.19–7.24 (m, 2H, 6,7-H), 7.40–7.43 (m, 1H, 8-H or 5-H). MS (m/z): 247(M^+, 4 %), 200 (37), 183 (40), 146 (40), 145 (32), 141 (61), 129 (59), 128 (67), 117 (57), 115 (84), 91 (100).

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