Synthesis of the Mononitrophenanthrenes.

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The mononitrophenanthrenes, apart from the 1- and the 9-isomer, have hitherto been obtained only by the nitration of phenanthrene. All five isomers have now been synthesised from the corresponding amines; in addition 2-nitrophenanthrene has been obtained by Wagner–Meerwein rearrangement of 2-nitro-9-fluorenylmethyl acetate. The properties of the 2- and the 4-isomer differ significantly from those described by previous workers.

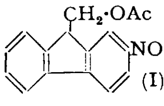
SCHMIDT and HEINLE (*Ber.*, 1911, **44**, 1488) studied the nitration of phenanthrene and claimed to have isolated from the reaction four isomeric mononitrophenanthrenes in the following proportions: 9-, 60%; 2-, 20%; 4-, 20%; 3-, 2%. They reported that, despite an intensive search, they could find no trace of the 1-isomer.

These results are very much at variance with predictions made by one of us (Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3357) on the basis of molecular-orbital theory, which suggest that the order of reactivity of the sites in phenanthrene should be $9 > 1 > 4 > 3 > 2$. However, separation of isomeric phenanthrene derivatives is often very difficult even with the use of modern techniques, so it seemed likely that Schmidt and Heinle's results were in error. This impression is supported by the properties reported by them for their mononitrophenanthrenes; for example, the 2-isomer was stated to be impure while the "4-isomer" was reduced to an amine of m. p. 105°, whereas authentic 4-aminophenanthrene, prepared later by Langenbeck and Weissenhorn (*Ber.*, 1939, **72**, 724), has m. p. 55°.

We therefore reinvestigated the nitration of phenanthrene, and as a preliminary, prepared all five mononitrophenanthrenes by unambiguous methods. Previously only the 1- and the 9-isomer had been synthesised (Hey and Osbond, *J.*, 1949, 3172; Cook and Moffatt, *J.*, 1951, 2487), the rest having been isolated by laborious fractional crystallisation from the mixtures of isomers formed in the nitration of phenanthrene.

The nitrophenanthrenes could be prepared from the corresponding aminophenanthrenes by treating the corresponding diazonium cobaltinitrites with " cupric nitrite " and freshly precipitated cuprous oxide (cf. Hodgson and Marsden, *J.*, 1944, 22). The yields were very poor (5—6%), but reproducible. The diazonium fluoroborates gave similar yields under the same conditions and, since they proved much easier to prepare, they have been used throughout. We found, in agreement with Hodgson and Marsden, that freshly precipitated cuprous oxide is essential for the formation of the nitro-compounds. Copper bronze, added under the same conditions or used alone, prevented the formation of nitro-compounds (cf. Starkey, *Org. Synth.*, Coll. Vol. II, p. 225).

We also obtained 2-nitrophenanthrene by a very much better method, based on the synthesis of phenanthrene by Wagner–Meerwein rearrangement of 9-fluorenylmethanol. Acetylation of 9-fluorenylmethanol with *iso*propenyl acetate gave the corresponding acetate, which could be nitrated in good yield to 2-nitro-9-fluorenylmethyl acetate (I). When this was heated with polyphosphoric acid, 2-nitrophenanthrene was formed in excellent yield. Attempts are being made to extend this method to the other nitrophenanthrenes and related compounds.



(I)

The melting points of the pure mononitrophenanthrenes are tabulated alongside those reported previously. It is curious that the m. p. reported by Schmidt and Heinle for the 4-isomer coincides with that found by us; the melting points of the amine (105°) and acetamido-derivative (190°) obtained by Schmidt and Heinle from their 4-isomer differ from those of pure 4-amino- (m. p. 55°) and 4-acetamido-phenanthrene (m. p. 203—204°). Our 1-nitrophenanthrene was identical with a specimen very kindly provided by Professor D. H. Hey.

	Melting point	
Nitrophenanthrene	This work	Previous work
1-	133°	133° [a]
2-	119—120	99 [b]
3-	172—174	171 [b]
4-	82	80—82 [b]
9-	118	118 [b]

[a] Hey and Osbond, *loc. cit.* [b] Schmidt and Heinle, *loc. cit.*; Cook and Moffatt, *loc. cit.*, report m. p. 113—114° for the 9-isomer.

EXPERIMENTAL

9-*Nitrophenanthrene*.—A solution of 9-aminophenanthrene (3 g.) (Bachmann and Boatner, *J. Amer. Chem. Soc.*, 1936, **58**, 2098) in dioxan (10 ml.) was added to a stirred ice-cold solution of hydrochloric acid (10 ml.) in water (100 ml.). A solution of sodium nitrite (1·25 g.) in water (5 ml.) was added in one portion and the solution stirred at 0° for ½ hr. Hydrofluoroboric acid (15 ml. of 40%) was added, and after a further ½ hour's stirring the yellow precipitate of 9-phenanthryldiazonium fluoroborate was collected and dried in a vacuum. The dry finely powdered fluoroborate was added gradually to a stirred mixture of sodium nitrite (20 g.), cupric sulphate (20 g.), freshly prepared cuprous oxide (5 g.), and water (400 ml.). Stirring was continued for 1 hr. and the mixture left overnight. Next day the organic material was extracted with chloroform (4 × 100 ml.), and the combined extracts were washed with water, dried and evaporated. The residual black tar was chromatographed from light petroleum on alumina, the pale yellow and least strongly adsorbed band being eluted. After a further chromatographic purification and successive crystallisations from light petroelum and ethanol, 9-nitrophenanthrene was obtained in pale yellow needles (0·26 g., 7·5%), m. p. 118° (Found : C, 75·4; H, 4·2; N, 6·3. Calc. for $C_{14}H_9O_2N$: C, 75·3; H, 4·1; N, 6·3%).

1-*Nitrophenanthrene*.—1-Aminophenanthrene (Langenbeck and Weissenhorn, *loc. cit.*) was converted into 1-nitrophenanthrene in 60% yield by the method used for the 9-isomer; chromatography from light petroleum on alumina and crystallisation from ethanol gave material of m. p. 133°, undepressed by a specimen prepared by Hey and Osbond (*loc. cit.*) and supplied to us by Professor D. H. Hey.

4-*Nitrophenanthrene*.—Prepared as above from β-2-naphthoylpropionic acid, 4-nitrophenanthrene crystallised from light petroleum in pale yellow prisms, m. p. 82° (Found : C, 75·7; H, 4·2; N, 6·1%). The yields in the Langenbeck–Weissenhorn reaction (12%), and in the conversion of the amine into the nitro-compound (1·7%), were very poor.

2-*Nitrophenanthrene*.—2-Acetylphenanthrene (Mosettig and van de Kamp, *J. Amer. Chem.*

Soc., 1930, **52**, 3704) was converted into 2-nitrophenanthrene by the method used for the 9-isomer. The nitro-compound, after chromatography from light petroleum on alumina, crystallised from 50% acetic acid in bright yellow needles (yield, 6%), m. p. 119—120° (Found: C, 75·4; H, 4·0; N, 6·25%).

3-*Nitrophenanthrene*.—Prepared in 5% yield by the method used for the 2-isomer, 3-nitrophenanthrene crystallised from light petroleum in pale yellow needles, m. p. 172—174°.

9-*Fluorenylmethyl Acetate*.—Pure 9-fluorenylmethanol (12·2 g.) (Burr, *ibid.*, 1951, **73**, 823) was boiled under reflux with *iso*propenyl acetate (140 g.) containing sulphuric acid (2 drops) for 2½ hr. Sodium hydrogen carbonate (1 g.) was then added, most of the solvent distilled off, and the residue diluted with light petroleum, treated with a little fuller's earth and evaporated. The residue crystallised from light petroleum, giving 9-fluorenylmethyl acetate (11·6 g., 80%) as prisms, m. p. 87° (lit., 84—85°) (Found: C, 80·6; H, 6·0. Calc. for $C_{16}H_{14}O_2$: C, 80·4; H, 5·9%). Treatment of a portion with polyphosphoric acid for 30 min. at 160—165° gave phenanthrene in good yield.

2-*Nitro*-9-*fluorenylmethyl Acetate*.—9-Fluorenylmethyl acetate (6·5 g.) was dissolved in warm acetic anhydride (20 ml.) and the solution cooled to 30—35°. Fuming nitric acid (1·45 ml.; *d* 1·5) in acetic anhydride (2 ml.) was added with shaking. After being kept at room temperature overnight, the solution was left at 0° for 24 hr. Pale yellow crystals separated and were collected (4·0 g., 52%). Recrystallisation from glacial acetic acid gave 2-*nitro*-9-*fluorenylmethyl acetate* as pale yellow prisms, m. p. 125—126° (Found: C, 67·6; H, 4·7; N, 5·0. $C_{16}H_{13}O_4N$ requires C, 67·8; H, 4·6; N, 4·95%). Dilution of the mother-liquors gave crystals of lower m. p. The nitro-ester was soluble in concentrated sulphuric acid to an orange solution. Attempted hydrolysis with ethanol–hydrochloric acid, or with potassium ethoxide–ethylene glycol, gave impure products. Fission of the ester group with hydrazine also gave an impure product.

2-*Nitrophenanthrene*.—The nitro-ester (1 g.) was added to hot, stirred polyphosphoric acid (50 ml.), and the resulting bright yellow solution kept at 160—165° for ½ hr. A dark oil separated. After cooling, the mixture was diluted with water and the solid collected and dried (0·7 g., 89%). Crystallisation from ethanol gave bright yellow needles, m. p. 120—121°, undepressed on admixture with 2-nitrophenanthrene.

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