ALIPHATIC CHEMISTRY OF FLUORENE

PART III. SOME DERIVATIVES OF FLUORENE AND PHENANTHRENE[1]

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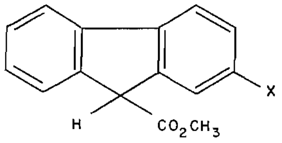
ABSTRACT

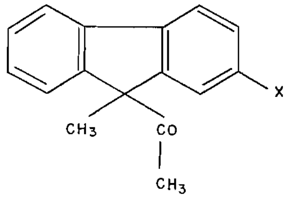
Methyl fluorene-9-carboxylate and 9-methyl-9-acetylfluorene have been nitrated and the products converted to 2-nitrophenanthrene and 2-nitro-9,10-dimethylphenanthrene, respectively.

Acetylation of 9,10-dimethylphenanthrene has given only one ketone, probably the 3-isomer. 4-Nitrofluorenone has been synthesized by a convenient route.

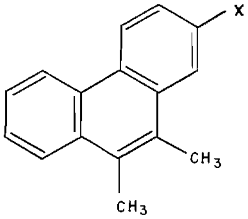
All five mononitrophenanthrenes have been synthesized (1) but only the 2-isomer is readily accessible (1, 2). Another closely related route to 2-nitrophenanthrene has now been found. Methyl 2-nitrofluorene-9-carboxylate (II), prepared by nitrating the ester (I), was reduced with lithium borohydride and the crude carbinol heated with polyphosphoric acid to give 2-nitrophenanthrene in 45% yield. In a similar way, 2-nitro-9,10-dimethylphenanthrene (VI) was prepared from 9-methyl-9-acetylfluorene (III) via the nitro-ketone (IV).



I, X = H
II, X = NO_2

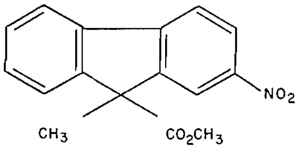


III, X = H
IV, X = NO_2

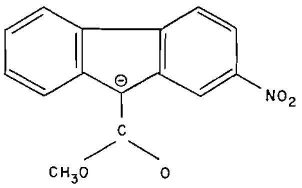


V, X = H
VI, X = NO_2
VII, X = NH_2
VIII, X = $NH\cdot CO\cdot CH_3$

During the isolation of the nitro-ester (II), it was noted that washing a chloroform solution of the nitration products with 2% sodium hydroxide solution resulted in the formation of a deep purple color, most easily observed by dissolving the pure nitro-ester in methanol containing sodium methoxide. Under the latter conditions, the color was rapidly discharged by methyl iodide with formation of what is considered to be the C-methyl derivative (IX) (cf. the alkylation of I (3)). The deep purple color was attributed to the anion (X) (cf. methyl fluorene-9-carboxylate anion (3)). These observations led directly to investigations of several aspects of the chemistry of fluorene (3, 4, 5) which are still in progress.



IX



X

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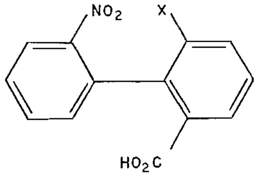
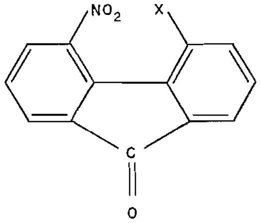
Contribution from the Chemistry Department, the University, Hull, East Yorkshire, England.

4-Nitrofluorenone (XIV) has been synthesized by the cyclization of the nitro-acid (XI) (cf. the acids XII and XIII which gave XV and XVI (6, 7)), but its conversion to 4-nitrofluorene, a desirable intermediate for the synthesis of the very inaccessible 4-nitrophenanthrene, was not achieved.



XI, X = H
XII, X = NO_2
XIII, X = CO_2H



XIV, X = H
XV, X = NO_2
XVI, X = CO_2H

The use of methyl fluorene-9-carboxylate as a synthetic tool has made several otherwise inaccessible hydrocarbons readily available (3, 8). One of these, 9,10-dimethylphenanthrene, has now been acetylated. Under homogeneous conditions in nitrobenzene at room temperature, only one ketone was isolated in 75–85% yield after reaction times of either 12 hours or 14 days. Prolonged efforts to degrade the ketone to the amine or carboxylic acid have failed. Attempts to synthesize reference compounds other than the amine (VII) have been unsuccessful but are reported in the Experimental section. The orientation of the *x*-acetyl-9,10-dimethylphenanthrene remains unestablished, but it is probably the 3-isomer by analogy with the acetylation of phenanthrene (9, 10 but see also Gore (11)).

9,10-Dimethylphenanthrene has been oxidized by aqueous sodium dichromate at 250° to phenanthrene-9,10-dicarboxylic acid (94%), 2-methyltriphenylene yielding the corresponding acid in 98% yield.* This technique should prove of great value in the preparation of derivatives of polycyclic hydrocarbons.

EXPERIMENTAL

2-Nitrophenanthrene

Methyl fluorene-9-carboxylate (2 g) was nitrated as described for 9-fluorenylmethyl acetate (1). *Methyl 2-nitrofluorene-9-carboxylate* crystallized from xylene–pentane as pale yellow needles (0.8 g), m.p. 178–179°. Found: C, 67.0; H, 4.31; N, 5.21%. Calc. for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20%. Less satisfactorily, 2-nitrofluorene-9-carboxylic acid (13) was esterified with methanolic hydrogen chloride.

The nitro-ester dissolved in methanol containing sodium methoxide to give a black solution, purple at high dilution. The color was rapidly discharged by methyl iodide with formation of *methyl 9-methyl-2-nitrofluorene-9-carboxylate*, pale yellow prisms from heptane, m.p. 122–123°. Found: C, 67.73; H, 4.19%. Calc. for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63%.

The nitro-ester (II) was reduced with lithium borohydride in tetrahydrofuran (14, 15) to give an orange resin. A part of the resin was acetylated with isopropenyl acetate (1) and the product purified by passing a hexane solution of it through a column of activated

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**The author is indebted to Dr. D. Fishel of the State University of South Dakota for these experiments (12, p. 22P).*

alumina. The eluted material crystallized as pale yellow prisms (22%) from hexane, m.p. 123–125°, not depressed by authentic 2-nitro-9-fluorenylmethyl acetate (1).

The other part of the resin was heated with polyphosphoric acid as described for 9-fluorenylmethyl acetate (1) to give 2-nitrophenanthrene as yellow needles from heptane (45%), m.p. 118–119°, not depressed by an authentic sample (1). Oxidation with periodic acid in boiling acetic acid gave 2-nitrophenanthraquinone, orange plates from acetic acid, m.p. 270–272°, not depressed by an authentic specimen (16). Found: C, 65.79; H, 2.60%. Calc. for $C_{14}H_7NO_4$: C, 66.41; H, 2.79%.

2-Nitro-9,10-dimethylphenanthrene

Pure 9-methyl-9-acetylfluorene (8) was nitrated as described for 9-fluorenylmethyl acetate (1). *2-Nitro-9-methyl-9-acetylfluorene* (70%) formed pale yellow prisms from methanol, m.p. 136–138°, raised to 138–139° by two further crystallizations. Found: C, 71.99; H, 5.19%. Calc. for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90%.

The *carbinol*, obtained as an oil by reducing the nitro-ketone with methanolic sodium borohydride, was esterified with *p*-toluenesulphonyl chloride in pyridine (3). The crude *tosylate* was boiled under reflux for 12 hours with 94% formic acid, *2-nitro-9,10-dimethylphenanthrene* crystallizing on cooling. Purification by passing a hexane solution of it through a column of activated alumina and concentration of the eluant gave bright yellow needles (74% based on nitro-ketone), m.p. 163–164°. Found: C, 76.75; H, 5.31%. Calc. for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.57%.

2-Amino-9,10-dimethylphenanthrene, prepared by reducing the nitro compound with hydrazine and palladized charcoal (17), crystallized as white needles from ethanol, m.p. 141–142°. The *N-acetyl* derivative crystallized from toluene as small white needles, m.p. 256–257°. A sample was sublimed at 220°/10^{-3} mm for analysis. Found: C, 82.16; H, 6.86%. Calc. for $C_{18}H_{17}NO$: C, 82.10; H, 6.51%.

4-Nitrofluorenone

2′-Nitrodiphenyl-2-carboxylic acid (18) (1.2 g) was maintained for 20 minutes at 115° with concentrated sulphuric acid (40 ml). Pouring onto ice precipitated a yellow solid, which crystallized from methanol (Norite) as long yellow needles (0.98 g), m.p. 173–174° (lit. m.p. 173–174° (19)).

9,10-Dimethylphenanthrene

Crude 9-acetylfluorene (20) (1 mole) was methylated with methyl iodide (2.1 moles) in methanol containing sodium methoxide (2 moles), the reaction being complete after 6 hours at room temperature. The crude ketone (96%, m.p. 82–84°) (lit. m.p. 85–86° (8)) was reduced with ethereal lithium aluminum hydride to 1′-(9-methyl-9-fluorenyl)-ethanol (98%, m.p. 77–80°) (lit. m.p. 81° (8)). The *tosylate*, prepared in the usual way (3), formed colorless prisms from chloroform–hexane, m.p. 88–90° with decomposition to 9,10-dimethylphenanthrene. Found: S, 8.62%. Calc. for $C_{23}H_{22}O_3S$: S, 8.47%.

9,10-Dimethylphenanthrene was prepared either by boiling the crude tosylate with 94% formic acid, or by boiling the carbinol with its own weight of phosphorus pentoxide in xylene for 2 hours. It formed long white needles (85–91%) from toluene–hexane, m.p. 143–144° (lit. m.p. 143–144° (8)).

Phenanthrene-9,10-dicarboxylic acid

9,10-Dimethylphenanthrene was oxidized by aqueous sodium dichromate solution at 250° (12), giving crude phenanthrene-9,10-dicarboxylic acid in 94% yield. The anhydride crystallized from acetic anhydride as pale yellow needles, m.p. 322–324°, not depressed by an authentic specimen (21).* The dimethyl ester formed pale yellow needles from benzene, m.p. 132–133° (lit. m.p. 131° (21)).

Triphenylene-2-carboxylic Acid

2-Methyltriphenylene (22), oxidized as above, gave triphenylene-2-carboxylic acid in 98% yield. The methyl ester crystallized as colorless needles from toluene, m.p. 129–130°. Found: C, 83.81, 84.01; H, 5.26, 5.34%. Calc. for $C_{20}H_{14}O_2$; C, 83.90; H, 4.93% (lit. m.p. 122–124° (23)).

x-Acetyl-9,10-dimethylphenanthrene

Anhydrous aluminum chloride (43 g, 2.2 moles) was dissolved in dry nitrobenzene (150 ml) and the solution cooled to 0°. 9,10-Dimethylphenanthrene (29.8 g, 1 mole) was added, followed by freshly distilled acetyl chloride (16 g, 1.4 moles). The mixture was left at room temperature for 14 days with exclusion of moisture. The complex was decomposed with ice and hydrochloric acid and the nitrobenzene removed by distillation with steam. Distillation of the residue at 1–2 mm gave the ketone as an almost colorless oil, which soon crystallized. One crystallization from acetone–methanol gave very pale yellow prisms (26 g, 73%), m.p. 108–110°. Fractional crystallization gave a further 4.5 g of ketone of the same melting point. A second ketone was not found.

The first crop of ketone was recrystallized once from methanol–acetone and twice from toluene–heptane to give colorless prisms (20 g, 56%), m.p. 111.5–112°. This melting point was not raised by further crystallizations. Found: C, 86.94; H, 6.55%. Calc. for $C_{18}H_{16}O$: C, 87.06; H, 6.50%.

The *oxime*, prepared in pyridine–ethanol, crystallized as white needles from toluene–heptane, m.p. 209–210°. OH stretching band (CS_2 solution) 3586 cm^{-1}. Found: C, 82.13; H, 6.65%. Calc. for $C_{18}H_{17}NO$: C, 82.11; H, 6.51%.

The *azine*, prepared by warming the ketone with hydrazine in ethanol, separated from xylene as golden-yellow plates, m.p. 280–281°. Found: C, 87.82; H, 6.41; N, 5.80%. Calc. for $C_{36}H_{32}N_2$: C, 87.77; H, 6.55; N, 5.69%.

x-Ethyl-9,10-dimethylphenanthrene was prepared by boiling the ketone (1 g) under reflux for 6 hours with hydrazine hydrate (10 ml) and diethylene glycol (100 ml). The purified hydrocarbon, obtained by passing a hexane solution of it through a column of activated alumina, crystallized from methanol as long white needles, m.p. 45.5–46°. Found: C, 92.32; H, 5.72%. Calc. for $C_{18}H_{18}$: C, 92.26; H, 5.74%. The 1,3,5-trinitrobenzene complex crystallized from methanol as bright yellow needles, m.p. 164–166°.

Numerous attempts to oxidize the ketone using aqueous sodium hypochlorite and pyridine or dioxane as diluent gave tars and only traces of acidic material. Reaction with sodium azide in acetic acid (24) also failed to yield useful products.

Reaction between the pure oxime and phosphorus pentachloride – benzene, hydrogen chloride – acetic acid or polyphosphoric acid gave uniformly low yields of mixtures, from which traces of an amine were obtained by hydrolysis with ethanolic hydrogen chloride. The amine rapidly turned red in air, behavior similar to that of 3-aminophenanthrene, and had an infrared spectrum markedly different from that of 2-amino-9,10-dimethylphenanthrene.

3-Ethylphenanthrene-9-carboxylic acid

3-Acetyl-9-bromophenanthrene (55 g, m.p. 151–153°) (lit. m.p. 150–151° (25)) was

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The author is indebted to I. Ungar of the Battelle Memorial Institute for this sample.

boiled under reflux for 4 hours with cuprous cyanide (20 g) and dimethylformamide (150 ml) containing 2 drops of pyridine. After cooling, the mixture was poured into concentrated aqueous ammonia and the precipitated solid crystallized from toluene, 3-acetyl-9-cyanophenanthrene (50 g) separating as yellow needles, m.p. 226–227° (lit. m.p. 220–221° (25)).

The nitrile (49 g) was boiled under reflux with hydrazine hydrate (40 ml) and diethylene glycol (300 ml). After 1 hour a solution of potassium hydroxide (40 g) in water (60 ml) was added dropwise. The mixture was distilled until a distillate temperature of 195° was reached. After a further 4 hours, the mixture was cooled and poured into excess dilute hydrochloric acid. The *acid* was collected, washed, and dissolved in 5% aqueous potassium carbonate solution and the solution filtered into dilute hydrochloric acid. The purified acid was dried and converted to the methyl ester by successive reactions with thionyl chloride and methanol. After distillation at 200–210° and 1–2 mm, the colorless ester was saponified, giving the acid as an oil which crystallized during several days. The yield was 20 g. Two crystallizations from methanol–acetone gave almost colorless needles, m.p. 180–182°, with previous sintering. Found: C, 82.30, 82.20; H, 5.57, 5.68%. Calc. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%.

3-Ethyl-9,10-phenanthraquinone

3-Acetylphenanthrene (9) was reduced to 3-ethylphenanthrene using hydrazine and diethylene glycol. The hydrocarbon, which has not been obtained crystalline (26), was distilled and purified through the picrate, which crystallized from methanol as orange needles, m.p. 120–121°. Oxidation with chromic oxide in acetic acid gave 3-ethylphenanthraquinone, slender orange needles from ethanol, m.p. 173–174° (lit. m.p. 168–170° (26)). Heating the quinone with potassium hydroxide in water or aqueous alcohol gave tars and only traces of acidic material.

3-Methylfluorene

Benzyl *p*-tolyl ketone (218 g, 55%) was prepared from phenylacetyl chloride (2 moles) and toluene, as described for benzyl phenyl ketone (27, p. 156). It formed plates from methanol, m.p. 109–110° (lit. m.p. 110–110.5° (28)). Found: C, 85.57; H, 6.88%. Calc. for $C_{15}H_{14}O$: C, 85.68; H, 6.71%. The *2,4-dinitrophenylhydrazone* formed irregular red prisms from benzene, m.p. 213–214°. Found: C, 64.45; H, 4.47%. Calc. for $C_{21}H_{18}N_4O_4$: C, 64.60; H, 4.65%.

The preceding desoxybenzoin was converted to 4-methylbenzoin* by a general procedure (29, p. 296) involving successively photobromination, reaction with sodium ethoxide, and hydrolysis with dilute hydrochloric acid. It crystallized from aqueous ethanol as long colorless needles (65%), m.p. 112–113° (lit. m.p. 110° (30)). Found: C, 79.81; H, 6.39%. Calc. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%.

Oxidation of the benzoin with cupric sulphate and pyridine (31, p. 715) gave 4-methylbenzil as a yellow oil, which largely crystallized after distillation (lit. m.p. 31° (32)). Conversion to 4-methylbenzilic acid proceeded in high yield (31, p. 715), but the acid proved remarkably difficult to crystallize. The yield of white needles from chloroform–hexane, m.p. 132–134°, was only 41% (lit. m.p. 132° (32)).

Cyclization of the benzilic acid has already been reported (34) but proceeds in higher yield by a more recent procedure (33). The crude dried 3-methylfluorene-9-carboxylic acid was decarboxylated by distillation at 1 mm, giving 3-methylfluorene in 43% yield

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**Primes (') are used for substituents on the ring adjacent to the carbinol group.*

based on the benzilic acid. It crystallized from methanol as colorless plates, m.p. 87–88° (lit. m.p. 88° (34)).

Prepared similarly, *benzyl p-ethylphenyl ketone* (71%) crystallized as lustrous colorless plates from methanol, m.p. 62–64°. Found: C, 85.41; H, 7.02%. Calc. for $C_{16}H_{16}O$: C, 85.67; H, 7.19%. The *2,4-dinitrophenylhydrazone* formed iridescent vermilion scales from benzene, m.p. 186–187°. Found: C, 65.10; H, 5.48%. Calc. for $C_{22}H_{20}N_4O_4$: C, 65.01; H, 5.48%.

4-Ethylbenzoin formed clusters of needles from heptane, m.p. 89–90°. Found: C, 79.91; H, 6.44%. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%. 4-Ethylbenzil and 4-ethylbenzilic acid have failed to crystallize and have not been characterized.

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