in an ice bath and was treated *carefully* with 20 ml. of water added dropwise. Ice-cold 1:1 hydrochloric acid (50 ml.) was added followed by a few drops of concentrated hydrochloric acid. The ether layer was removed, and the clear aqueous phase was extracted several times with ether. The combined ether solutions were washed with portions of water until the washings were neutral and were then dried over sodium sulfate. Complete removal of solvent left 0.49 g. (96%) of crude 4-hydrox-1,2,8,10-tetramethyl-1,2,3,4-tetrahydrophenanthrene. No absorption was evident at 5.98 μ; hydroxylic absorption was evident at 3.0 μ.

This crude material (0.48 g., 1.9 mmoles) was mixed with 0.28 g. of 10% palladium-on-charcoal (American Platinum Works) in a 20-ml. test tube fitted with an air condenser. The mixture was held in a bath at 280–290° for 1 hr. and then at 300–310° for 0.5 hr. The dehydrogenation mixture was extracted with several portions of anhydrous ether, and material that did not dissolve was rejected. Removal of all solvent gave 0.42 g. of partially crystalline product II.

A solution of the crude material in 40 ml. of petroleum ether (Reagent, b.p. 30–60°) followed by 100 ml. of the same solvent was passed through a 13 × 1 cm. column of activated alumina (Fisher Adsorption Alumina, 80–200 mesh; 9 g.). Evaporation of solvent from the emergent solution left 0.39 g. of pale yellow, waxy needles. Repetition of the cromatographic process yelded 0.35 g. of colorless product. Two crystallizations from methanol gave tiny white needles (0.21 g.; 46%) of 1,2,8,10-tetramethylphenanthrene (II), m.p. 108–110.5°. The sample prepared for analysis by another crystallization melted at 109.5–110.5°.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.44; H. 7.86.

The ultraviolet absorption spectrum of 1,2,8,10-tetramethylphenanthrene (II) as a 0.1×10^{-4} to $8 \times 10^{-4}M$ alcohol (95%) solution showed the following maxima: 358 mμ (log ϵ 2.36), 351 (1.55), 342 (2.55), 336 sh (2.11), 311 (4.18), 298 (4.15), 286 sh. (4.16), 264 (4.81), 257 sh (4.74), 228 sh (4.33), 217.3 (4.61). The ultraviolet absorption curve matched the one observed for the same phenanthrene obtained as a derivative of cassaic acid.[7]

Three derivatives of 1,2,8,10-tetramehylphenanthrene (II) were prepared. According to the general directions of Vogel,[39] 30 mg. of the phenanthrene was combined with 28 mg. of 1,3,5-trinitrobenzene in absolute ethanol to give a bright yellow precipitate. Recrystallizations, once from absolute ethanol and twice from absolute ethanol-chloroform, furnished the trinitrobenzene derivative of 1,2,8,10-tetramethylphenanthrene (II) as bright yellow needles, m.p. 164–165°.

Anal. Calcd. for $C_{24}H_{21}O_6N_3$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.54; H, 4.67; N, 9.25.

The picrate derivative was prepared[39] by allowing a solution of 20 mg. of phenanthrene II and 25 mg. of picric acid in 4.5 ml. of 95% alcohol to stand at room temperature. Filtration afforded orange-red needles of the desired picrate, which was washed with a few drops of cold alcohol and then dried for two days in vacuo over phosphorus pentoxide. The melting point of the picrate was 141.5–142.5°.

Anal. Calcd. for $C_{24}H_{21}O_7N_3$: C, 62.20; H, 4.57; N, 9.07. Found: C, 62.48; H, 4.70; N, 8.91.

The trinitrofluorenone derivative was prepared[40] by allowing a solution of 24 mg. of 1,2,8,10-tetramethylphenanthrene (II) and 32 mg. of 2,4,7-trinitrofluorenone in a small volume of absolute ethanol to stand at room temperature for 0.5 hours. The precipitated deep orange-red solid was collected, washed with a few drops of cold absolute ethanol, and dried. Two crystallizations of the product from anhydrous benzene-ethanol gave the desired derivative in the form of dark orange-red clusters of needles melting at 166–167°.

Anal. Calcd. for $C_{31}H_{23}O_7N_3$: C, 67.75; H, 4.22; N, 7.65. Found: C, 67.89; H, 4.29; N, 7.74.

Interestingly, when the trinitrofluorenone derivative was brought out of *dilute* solution, the color of the deposited crystals was a much lighter orange. However, the melting point was the same (166–168°), and the melting point of a mixture (166–167°) of the two different colored materials was not depressed.

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BOSTON 15, MASS.

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[CONTRIBUTION FROM THE EVANS CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Syntheses of 3-Fluoro- and 4'-Fluoro-9,10-dimethyl-1,2-benzanthracene[1]

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The syntheses of 9,10-dimethyl-1,2-benzanthracene and of 4'-fluoro- and 3-fluoro-9,10-dimethyl-1,2-benzanthracenes are described.

The reasons for synthesis of fluoro derivatives of 9,10-dimethyl-1,2-benzanthracene for studies on carcinogenic activity have been presented.[2] In this paper a modified synthesis of 9,10-dimethyl-1,2-benzanthracene[3–7] is described and the syntheses

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[1] This work was supported by a grant from the National Institutes of Health.

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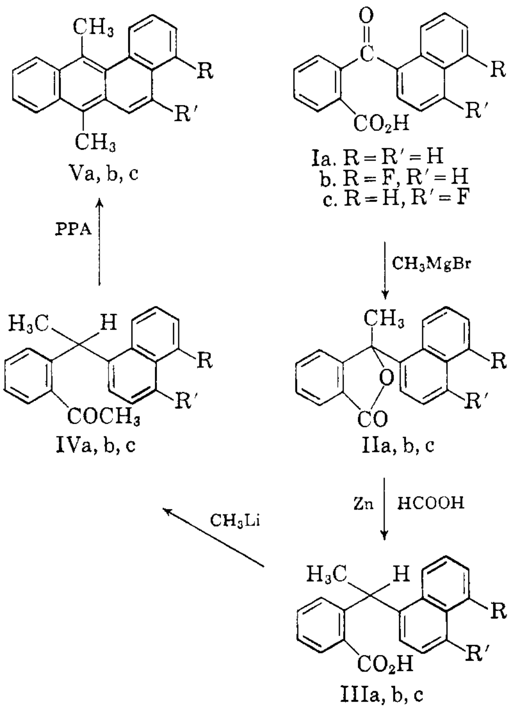
of 3-fluoro- and 4′-fluoro-9,10-dimethyl-1,2-benzanthracene have been completed by the sequence of reactions outlined below.



The lactone IIa was formed in much better yield (61%) by treatment of Ia with methylmagnesium bromide[8] than by treatment of methyl and *i*-propyl *o*-acetylbenzoates with 1-naphthylmagnesium bromide (24 and 0%, respectively). The other lactones—IIb and IIc—were formed similarly from Ib and Ic in 56 and 79% yields. In the reduction of the lactones, IIa, b, and c, to the acids, IIIa, b, and c, better yields (near 90%) were obtained using zinc and formic acid[9] than by zinc-alkali reduction.[10]

The yields in conversion of the acids, IIIa, b, and c, to the corresponding methyl ketones, IVa, b, and c, by reaction with methyllithium were good and cyclization of these to the final products, Va, b, and c, was effected in high yields by heating with polyphosphoric acid (PPA).[11]

EXPERIMENTAL[12]

Methyl o-acetylbenzoate. A mixture of 9.84 g. of *o*-acetylbenzoic acid,[13] 10.2 g. of methyl iodide, 19.9 g. of potassium carbonate, and 200 ml. of acetone was refluxed with stirring for 1 day. After removal of insoluble materials by filtration, the solvent was distilled, the residue was diluted with 100 ml. of ether and worked up in the usual way.[14] After removal of the solvent, the residue was distilled to give 7.05 g. (66%) of the normal ester, b.p. 127–129° at 8 mm. (infrared absorption at 5.90 μ).

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.4; H, 5.6. Found: C, 67.4; H, 5.8.

Isopropyl o-acetylbenzoate. A mixture of 30.0 g. of *o*-acetylbenzoic acid, 34.5 g. of isopropyl iodide, 60.8 g. of potassium carbonate, and 600 ml. of 2-butanone was refluxed with stirring for 1 day. By a work-up similar to the above methyl ester there was obtained 33.0 g. (87%) of the normal ester, b.p. 152–153° at 8 mm. (infrared 5.90 μ).

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.9; H, 6.8. Found: C, 70.1; H, 6.9.

3-Methyl-3-(1-naphthyl)phthalide IIa. The phthalide, IIa, was prepared in 61% yield as described.[8]

Treatment of methyl *o*-acetylbenzoate with 1-naphthylmagnesium bromide in ether and benzene under reflux for 2 hr. afforded the IIa in 24% yield. No phthalide was obtained on reaction of isopropyl *o*-acetylbenzoate with 1-naphthylmagnesium bromide in ether and benzene under reflux for 2 hr.

o-(α-1-Naphthylethyl)benzoic acid (IIIa). A mixture of 2.0 g. of IIa, 30 g. of 90% formic acid,[9] 4 g. of zinc dust, and 4 ml. of water was refluxed for 12 hr. The reaction mixture was diluted with 200 ml. of water and the solids were collected with 300 ml. of 2% sodium hydroxide solution. After filtration, acidification with hydrochloric acid afforded 1.96 g. (97%) of colorless acid, IIIa, m.p. 167–168°, (lit.[8] 168–169°), suitable for use in the next reaction.

o-(α-1-Naphthylethyl)acetophenone (IVa). To a stirred solution of methyllithium prepared from 1.50 g. of lithium and 15.0 g. of methyl iodide in 90 ml. of ether was added dropwise a solution of 5.52 g. of IIIa in 100 ml. of ether. After the addition was complete, the mixture was stirred for 1 hr. at room temperature and then poured on ice. After isolation in the usual manner, the crude methyl ketone, IVa (4.73 g.) was obtained as white plates on removal of the solvent. Recrystallization from ethanol gave 4.07 g. (75%) of colorless plates, m.p. 113–114°. The analytical sample, obtained by recrystallization from ethanol, melted at 114–115°.

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.6; H, 6.6. Found; C, 87.5; H, 6.6.

9,10-Dimethyl-1,2-benzanthracene (Va). A mixture of 2.50 g. of the methyl ketone (IVa) and 30 g. of polyphosphoric acid (PPA) was heated with stirring at 95° for 1 hr. The reaction mixture was diluted with water and the yellow solid which precipitated (2.45 g., m.p. 120–122°) was collected, washed with water, and dried. By chromatography in benzene–Skellysolve B (petroleum ether, b.p. (65–70°) over alumina there was obtained 2.05 g. (87%) of Va, as pale yellow plates, m.p. 122–123°, not depressed by mixing with authentic sample.[7]

3-Methyl-3-(5-fluoro-1-naphthyl)phthalide (IIb). To a stirred solution of 11.7 g. of *o*-(5-fluoro-1-naphthoyl)benzoic acid,[2] Ib, in 200 ml. of ether and 250 ml. of benzene, there was added dropwise 50 ml. of 2.9*N* methylmagnesium bromide in ether. After two hours of refluxing, the mixture was decomposed with dilute hydrochloric acid. From the neutral fraction, freed of acids by washing with potassium

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(11) Compare C. K. Bradsher, *J. Am. Chem. Soc.*, **62**, 486 (1940).

(12) All melting points and boiling points are uncorrected. Microanalyses by Schwarzkopf Microanalytical Laboratory, 56-19 37th Avenue, Woodside 77, N. Y.

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(14) Reaction mixtures in general were taken up in ether-benzene mixtures, washed with dilute acid and/or potassium carbonate solutions, with saturated sodium chloride solution and were then dried by passage through a filter containing powdered anhydrous magnesium sulfate.

carbonate solution, was obtained 6.52 g. (56%) of IIb as colorless plates, m.p. 128–129°. An analytical sample, obtained by recrystallization from methanol, melted at 131–132°.

Anal. Calcd. for $C_{19}H_{13}FO_2$: C, 78.1; H, 4.5; F, 6.5. Found: C, 78.0; H, 4.5; F, 6.3.

o-(α-5-Fluoro-1-naphthylethyl)benzoic acid (IIIb). A mixture of 10.27 g. of IIb 20.6 g. of zinc dust, 206 ml. of formic acid and 21 ml. of water was refluxed for 12 hr. After dilution with 500 ml. of water the solids were collected and extracted with 300 ml. of 2% sodium hydroxide solution. After removal of insoluble materials, acidification afforded 10.15 g. of almost colorless IIIb. Recrystallization from benzene-Skellysolve B (1:1) gave 9.74 g. (94%) of IIIb as white needles, m.p. 160–161°. An analytical sample, obtained by recrystallization from benzene–Skellysolve B, melted at 161–162°.

Anal. Calcd. for $C_{19}H_{15}FO_2$: C, 77.5; H, 5.2; F, 6.5. Found: C, 77.9; H, 5.3; F, 6.4.

Reduction of IIb by the alkaline zinc dust method[10] afforded IIIb in 70% yield.

o-(α-5-Fluoro-1-naphthylethyl)acetophenone (IVb). Just as in the case of IIIa→IVa above described, 10.64 g. of IIIb was converted into 6.40 g. of crude IVb, m.p. 81–83°. Recrystallization from ethanol gave 6.10 g. (57%) of colorless prisms of IVb, m.p. 83–84°. An analytical sample, obtained by recrystallization from ethanol, melted at 84–85°.

Anal. Calcd. for $C_{20}H_{17}FO$: C, 82.1; H, 5.9; F, 6.5. Found: C, 82.1; H, 6.0; F, 6.3.

From the acid fraction, 2.96 g. (28%) of IIIb, m.p. 155–156°, was recovered.

4′-Fluoro-9,10-dimethyl-1,2-benzanthracene (Vb). A mixture of 6.10 g. of the methyl ketone, IVb, and 100 g. of polyphosphoric acid was heated with stirring at 85–90° for 1 hr. The reaction mixture was diluted with ice water and the yellow solid which precipitated was collected, washed with water, and dried. By chromatography in benzene–Skellysolve B (1:1) over alumina, there was obtained 5.27 g. (92%) of Va, as faintly colored plates, m.p. 97–98°. Further purification by chromatography afforded pure hydrocarbon, m.p. 97.5–98.0°.

Anal. Calcd. for $C_{20}H_{15}F$: C, 87.6; H, 5.5; F, 6.9. Found: C, 87.6; H, 5.6; F, 6.7.

3-Methyl-3-(4-fluoro-1-naphthyl)phthalide (IIc). To a stirred solution of 15.24 g. of o-(4-fluoro-1-naphthoyl)benzoic acid,[2] Ic, in 380 ml. of ether, was added dropwise 56 ml. of 3.0*N* methylmagnesium bromide in ether. After 2 hr. of refluxing, the mixture was decomposed with dilute hydrochloric acid. From the neutral fraction, freed of acids by washing with potassium carbonate, was obtained 13.45 g. (88%) of colorless plates, m.p. 126–130°. By recrystallization from ethanol, there was obtained 12.10 g. (79%) of IIc as colorless plates, m.p. 134–136°. An analytical sample, obtained by recrystallization from ethanol, melted at 143–144°, with little loss. Evidently, the lower melting form was polymorphic with the higher melting form.

Anal. Calcd. for $C_{19}H_{13}FO_2$: C, 78.1; H, 4.5; F, 6.5. Found: C, 78.2; H, 4.7; F, 6.4.

o-(α-4-Fluoro-1-naphthylethyl)benzoic acid (IIIc). A mixture of 5.10 g. of IIc, 10.2 g. of zinc dust, 100 ml. of 90% formic acid, and 10 ml. of water was refluxed for 12 hr. After isolation as described for IIIb there was obtained 5.05 g. of almost colorless IIIc. Recrystallization from benzene-Skellysolve B (1:1) gave 4.50 g. (88%) of IIIc as white needles, m.p. 163–164°.

Anal. Calcd. for $C_{19}H_{15}FO_2$: C, 77.5; H, 5.2; F, 6.5. Found: C, 77.8; H, 5.3; F, 6.2.

o-(α-4-Fluoro-1-naphthylethyl)acetophenone (IVc). Just as in the case of IIIa–IVa above described, 9.03 g. of IIIc was converted into 7.50 g. of IVc, colorless plates, m.p. 131–133°. Recrystallization from ethanol gave 7.10 g. (79%) of IVc, m.p. 133–134°. An analytical sample, obtained by recrystallization from ethanol, melted at 134–135°.

Anal. Calcd. for $C_{20}H_{17}FO$: C, 82.1; H, 5.9; F, 6.5. Found: C, 81.9; H, 5.9; F, 6.3.

From the acid fraction, 0.43 g. of IIIc, m.p. 161–163°, was recovered.

3-Fluoro-9,10-dimethyl-1,2-benzanthracene (Vc) A mixture of 6.00 g. of the methyl ketone (IVc) and 110 g. of polyphosphoric acid was heated with stirring at 85–90° for 1.5 hr. The reaction mixture was diluted with ice water and the hydrocarbon was extracted with ether. Chromatography in benzene–Skellysolve B under nitrogen over alumina afforded 3.70 g. (66%) of slightly yellow plates, m.p. 88–91°. By further chromatography, there was obtained 3.30 g. (59%) of pure Vc, as faintly colored plates, m.p. 92.5–93.0°. The purification must be carried out under nitrogen and/or in absence of sunlight to avoid formation of a peroxide which is apparently formed more easily from Vc than from Va or Vb.

Anal. Calcd. for $C_{20}H_{15}F$: C, 87.6; H, 5.5; F, 6.9. Found: C, 87.6; H, 5.6; F, 6.7.

3-Fluoro-9,10-dimethyl-1,2-benzanthracene peroxide. The compound, Vc (0.60 g.) was dissolved in benzene–Skellysolve B (1:1) and chromatographed over alumina with no precautions to exclude air or light. The eluate was evaporated to yield 0.54 g. of colorless plates, m.p. 91–150°. By fractional recrystallization from benzene–Skellysolve B (1:1), there was obtained 0.41 g. of the peroxide, m.p. near 206°, with decomposition.

Anal. Calcd. for $C_{20}H_{15}FO_2$: C, 78.4; H, 4.9; F, 6.2. Found: C, 78.2; H, 4.8; F, 6.3.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEMPLE UNIVERSITY]

Substituted 1,10-Phenanthrolines, XII. Benzo and Pyrido Derivatives[1]

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Received June 22, 1961

The synthesis of the following fused ring compounds is described—benzo [*b*]- and[*f*][1,10]phenanthrolines and the 5,6,-7,8-tetrahydro derivative of the latter; pyrido [3,2-*f*][1,7]phenanthroline; quino[8,7-*b*][1,10] phenanthroline.

It has been shown by analytical tests that 5,6-dimethyl-(I) and diethyl-1,10-phenanthroline, previously prepared in this laboratory, are sensitive reagents for the detection of Fe(II). The object of the present work was to provide 1,10-phenanthrolines with six-membered rings fused across the 5 and 6 positions.

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