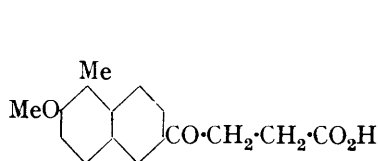


69. *Syntheses in the Phenanthrene Series. Part I. 2-Methoxy-1-methylphenanthrene.*

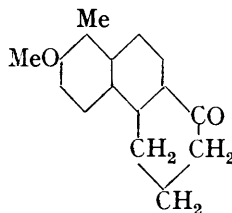
By PETER HILL, W. F. SHORT, and (in part) ALICE HIGGINBOTTOM.

THE object of the present series of investigations was the synthetic preparation of various phenanthrene derivatives related to members of the diterpene group which are under investigation in these laboratories. For the preparation of these compounds, we have extended and adapted the phenanthrene syntheses of (1) Schroeter (*Ber.*, 1929, **62**, 645), the requisite naphthoylpropionic acid being prepared by the modification of Giua's method so successfully exploited by Haworth and his co-workers, and (2) Bogert and Cook, and two new methods for constructing the phenanthrene ring system have been developed.

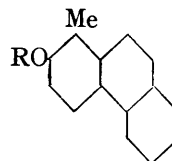
1-Methyl-2-naphthyl methyl ether was obtained by the action of methyl sulphate on the Grignard compound of 1-bromo-2-methoxynaphthalene (Franzen and Stäuble, *J. pr. Chem.*, 1921, **103**, 352), but is more conveniently prepared in quantity from 2:2'-dihydroxydi- α -naphthylmethane (Fries and Hübner, *Ber.*, 1906, **39**, 439). This methyl ether and succinic anhydride react in nitrobenzene solution in presence of aluminium chloride to afford β -(2-methoxy-1-methyl-6-naphthoyl)propionic acid (I) in 78% yield. The constitution assigned to this acid rests upon the observation that the final product (III; R = H) of the synthesis affords 1-methylphenanthrene when distilled with zinc dust, and the succinic anhydride must therefore have reacted in position 5 or 6. Further, contrary to the statement of Fieser and Peters (*J. Amer. Chem. Soc.*, 1932, **54**, 4351), condensation of β -naphthyl methyl ether with succinic anhydride under similar conditions affords β -(2-methoxy-6-naphthoyl)propionic acid as main product (following paper).



(I.)



(II.)



(III.)

Reduction of the keto-acid by Clemmensen's method furnished γ -(2-methoxy-1-methyl-6-naphthyl)butyric acid, from which 1-keto-7-methoxy-8-methyl-1:2:3:4-tetrahydrophenanthrene (II) was obtained by the action of stannic chloride. This ketone was reduced by Clemmensen's method, and the product dehydrogenated with selenium to yield 2-methoxy-1-methylphenanthrene (III; R = Me).

EXPERIMENTAL.

1-Methyl-2-naphthyl Methyl Ether.—Redistilled methyl sulphate (2 mols.) was added to a Grignard solution prepared from 1-bromo-2-methoxynaphthalene (1 mol.), methyl iodide (1 mol.), magnesium (2 atoms), ether (6 mols.), and an equal volume of dry benzene, and the mixture boiled for 2 hours. Distillation of the product afforded (1) a fraction, b. p. 160–165°/20 mm., m. p. 35–42°, consisting of the required ether and a small quantity of β -naphthyl methyl ether (which may be removed by crystallisation from methyl alcohol), and (2) a small higher-boiling fraction consisting of unchanged 1-bromo-2-methoxynaphthalene.

The preparation and reduction of 2:2'-dihydroxydi- α -naphthylmethane were conducted as described by Fries and Hübner (*loc. cit.*), but the tedious separation of the two phenols by means

of boiling water was avoided either by acetylation or by methylation. The mixed acetates, obtained by acetylation with acetic anhydride and sodium hydroxide at 0°, were extracted with boiling light petroleum (b. p. 40—60°), in which only 1-methyl-2-naphthyl acetate (m. p. 65°) dissolved, and the acetate was smoothly hydrolysed by boiling with dilute sodium hydroxide solution. Alternatively, methyl sulphate was rapidly added to a well-stirred solution of the mixed phenols in 15% aqueous potassium hydroxide so that the temperature did not exceed 70°. The portion of the product sparingly soluble in ether consisted of 2 : 2'-dimethoxydi- α -naphthylmethane (m. p. 144°), and distillation of the soluble portion removed the remaining traces of this compound together with some resin and afforded almost pure 1-methyl-2-naphthyl methyl ether (b. p. ca. 140°/5 mm.; m. p. 39·5—40·5°).

β -(2-Methoxy-1-methyl-6-naphthyl)propionic Acid (I).—Succinic anhydride (1·2 mols.) and 1-methyl-2-naphthyl methyl ether (1 mol.) were added below 5° to a mechanically stirred solution of aluminium chloride (2 mols.) in nitrobenzene (9 mols.). The mixture was slowly warmed to room temperature with stirring and then kept. The yield of keto-acid after 40 hours was 41%, but could be raised to 63% and 78% by increasing the period of reaction to 3 and 5 days respectively. The solution was decomposed with ice and hydrochloric acid, the nitrobenzene removed in steam and the solid residue washed with water and recrystallised from methyl alcohol. The acid (I) was obtained in colourless plates, m. p. 161—162° (Found: C, 70·4; H, 6·0. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%).

γ -(2-Methoxy-1-methyl-6-naphthyl)butyric Acid.—The keto-acid (20 g.) was reduced by gentle boiling for 12 hours with amalgamated zinc (100 g.) and concentrated hydrochloric acid (100 c.c.), and extraction of the acid cake with boiling ligroin furnished the pure acid, m. p. 123—123·5°, in 53% yield (Found: C, 74·5; H, 6·9. $C_{16}H_{18}O_3$ requires C, 74·4; H, 7·0%).

1-Keto-7-methoxy-8-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (II).—The preceding acid (48 g.) was slowly added with mechanical stirring to stannic chloride (96 c.c.) at 40—50°, the temperature being subsequently maintained at 105—110° for 70 minutes. The black product was decomposed with ice and hydrochloric acid and extracted with ether. When the solution was washed with dilute aqueous sodium hydroxide the colour disappeared, and stout yellow prisms of an acid, m. p. 194—195°, were obtained from the alkaline liquor; these were not further investigated. The ethereal solution deposited the ketone on concentration, and a further quantity was obtained by distilling the mother-liquor under diminished pressure, the fraction, b. p. 210—225°/2 mm., being almost pure. The cyclic ketone (II) separated from alcohol in colourless plates, m. p. 107° (Found: C, 80·0; H, 6·75. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%). The yield was variable (34—77%). The 2:4-dinitrophenylhydrazone separated from ethyl acetate in bright red, stout needles, m. p. 281° (Found: N, 13·2. $C_{22}H_{20}O_5N_4$ requires N, 13·3%).

7-Methoxy-8-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene.—Reduction of the cyclic ketone with sodium and absolute alcohol yielded an amorphous red substance. The ketone (13·2 g.), amalgamated zinc (67 g.), and concentrated hydrochloric acid (67 c.c.) were boiled for 10 hours, and the product distilled to remove resinous material. The fraction (4·5 g.), b. p. 170—185°/0·2 mm., on recrystallisation from alcohol furnished the pure tetrahydrophenanthrene, m. p. 111—112° (Found: C, 85·0; H, 8·15. $C_{16}H_{18}O$ requires C, 85·0; H, 7·95%).

2-Methoxy-1-methylphenanthrene, obtained by dehydrogenation with selenium, separated from chloroform-light petroleum in small colourless plates, m. p. 161° (Found: C, 86·4; H, 6·2. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%). The picrate consisted of orange-red needles, m. p. ca. 125—126°, but was too unstable for satisfactory recrystallisation. The methyl ether (1 g.) was smoothly demethylated on boiling (4 hrs.) with hydrobromic acid (45 c.c., *d* 1·5) and acetic acid (45 c.c.); the resulting 2-hydroxy-1-methylphenanthrene crystallised from methyl alcohol in irregular plates, m. p. 196—197° (Found: C, 86·5; H, 5·8. $C_{15}H_{12}O$ requires C, 86·5; H, 5·7%). Distillation of the phenol (0·4 g.) with a large excess of zinc dust in a combustion tube afforded a semi-solid distillate, which was dissolved in ether, washed with dilute alkali solution, and distilled from sodium under diminished pressure. The distillate melted at 121° after recrystallisation from light petroleum at 0° and did not depress the m. p. of a synthetic specimen of 1-methylphenanthrene (Sherwood and Short, *Rep. Austral. Assoc. Sci.*, 1933, 31, 38). The picrates of the two hydrocarbons also showed no depression in m. p. (137·5°). Small crystals of this picrate are almost pure yellow, but larger crystals have a red tinge.

4-Methylphenanthrene (A correction).—Radcliffe, Sherwood, and Short (J., 1931, 2293) published a synthesis of 4-methylphenanthrene and described the hydrocarbon as a solid, m. p. 117°. Soon afterwards, Dr. R. D. Haworth informed us privately that a similar synthesis had yielded 4-methylphenanthrene, m. p. 49—50°. Examination of the original preparations showed that, owing to an unfortunate confusion of specimens, we had ascribed the properties of 1-methyl-

phenanthrene (obtained from podocarpic acid) to 4-methylphenanthrene. The synthetic hydrocarbon melted at 49—50° and Dr. Haworth reported that it did not depress the m. p. of his preparation. He subsequently repeated our synthesis (J., 1932, 1127) and confirmed our description of all the intermediate products.

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