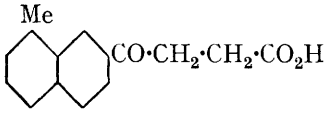
428. *Synthesis of Alkylphenanthrenes. Part VIII. Attempted Synthesis of 4 : 5-Dimethylphenanthrene.*

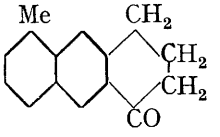
By Robert D. Haworth and George Sheldrick.

An attempt to synthesise 4 : 5-dimethylphenanthrene has led to an abnormal but not unexpected result. β-(8-*Methyl*-2-*naphthoyl*)*propionic acid* (I), prepared by a tedious method described in the experimental section, was reduced by Clemmensen's method, and the product cyclised. Theoretically, either the ketotetrahydroanthracene (II) or the ketotetrahydrophenanthrene (III) could be produced by this reaction. Although Schroeter (*Ber.*, 1921, **54**, 2243) and Krollpfeiffer and Schafer (*ibid.*, 1923, **56**, 628) obtained 1-ketooctahydroanthracene from γ-(2-tetralyl)butyric acid, the cyclisations carried out in previous parts of this series have led, without exception, to ketotetrahydrophenanthrenes. In the present case, cyclisation was effected with difficulty : no neutral product was obtained with sulphuric acid or stannic chloride as condensing agent, and the best result was a 15% yield, obtained by the action of aluminium chloride on the chloride of the Clemmensen reduction product of (I). The oily product, probably impure 1-*keto*-5-*methyl*-1 : 2 : 3 : 4-

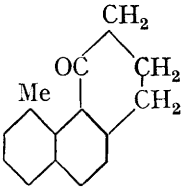
tetrahydroanthracene (II), was condensed with methylmagnesium iodide, and the product dehydrated and dehydrogenated. 1 : 5-*Dimethylanthracene* was obtained as a pale yellow, crystalline compound, and the structure was supported by converting the hydrocarbon into a scarlet *picrate*, and into a pale yellow *quinone*, which did not react with *o*-phenylenediamine.



(I.)



(II.)



(III.)

The formation of (II) by the cyclisation can be explained on steric grounds. A diagram drawn to scale shows the inhibiting influence of the methyl group on the formation of the ketotetrahydrophenanthrene (III) : a similar diagram shows that it is impossible to introduce two methyl groups in the 4 : 5-positions of phenanthrene without introducing excessive strain in the molecule.

Experimental.

β-*p*-Methoxybenzoylpropionic acid, m. p. 147—148° (Found : equiv., 210. Calc. for $C_{11}H_{12}O_4$: equiv., 208), was obtained in almost theoretical yield by the action of aluminium chloride on succinic anhydride and anisole in nitrobenzene solution.

γ-p-*Methoxyphenylbutyric Acid.*—β-*p*-Methoxybenzoylpropionic acid (60 g.), amalgamated zinc (300 g.), and concentrated hydrochloric acid (100 c.c.) were heated to boiling, and a further quantity (200 c.c.) of concentrated hydrochloric acid was added to the boiling solution during 4½ hours. The crude product, isolated with ether, was esterified with methyl-alcoholic hydrogen chloride and distilled. The fraction, b. p. 130—145°/0·5 mm., was hydrolysed with methyl-alcoholic potassium hydroxide; the acid crystallised from light petroleum (b. p. 60—80°) in colourless needles (40 g.), m. p. 63—64° (Found : equiv., 196. Calc. for $C_{11}H_{14}O_3$: equiv., 194).

1-*Keto*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene.*—Pure γ-*p*-methoxyphenylbutyric acid (40 g.) and thionyl chloride (40 c.c.) were gently refluxed for 1 hour, and the excess of thionyl chloride was removed under diminished pressure. The residue was dissolved in tetrachloroethane (200 c.c.), cooled to — 5°, and finely powdered aluminium chloride (52 g.) added gradually with stirring. After standing for 12 hours at room temperature, the mixture was decomposed with ice and hydrochloric acid, the tetrachloroethane removed in steam, and the residue extracted with ether. The extract was washed, first with water, then with dilute sodium hydroxide solution, dried, the solvent removed, and the residue distilled. The cyclic ketone (30 g.), b. p. 130—135°/0·5 mm., crystallised from light petroleum (b. p. 60—80°) in colourless plates, m. p. 66—67° (Found : C, 74·8; H, 6·9. Calc. for $C_{11}H_{12}O_2$: C, 75·0; H, 6·8%). During the course of this work Veselý and Štursa (*Coll. Czech. Chem. Comm.*, 1933, **4**, 170) described the preparation of this cyclic ketone by another method. They also converted it into 7-amino-1-methylnaphthalene on a small scale, and the experimental details given below are suitable for the preparation of larger quantities of the amine.

7-*Methoxy*-1-*methylnaphthalene.*—A solution of methylmagnesium iodide (prepared from magnesium, 4·5 g., and methyl iodide, 27 g., in ether, 100 c.c.) was added to a solution of the above cyclic ketone (26 g.) in ether (100 c.c.); after boiling for 1½ hours, the mixture was decomposed with sulphuric acid, and the product distilled. The distillate (23·4 g.), b. p. 158—160°/15 mm., was heated with selenium (24 g.); the temperature was raised from 220° to 275° during 5 hours, then raised to 290—295°, where it was maintained for 18 hours. The product, isolated with chloroform, boiled at 159—161°/15 mm. and separated from light petroleum (b. p. 60—80°) in colourless plates (22·5 g.), m. p. 47—48° (Found : C, 83·7; H, 7·1. Calc. for $C_{12}H_{12}O$: C, 83·7; H, 7·0%).

7-*Hydroxy*-1-*methylnaphthalene.*—The above methyl ether (68 g.), hydrobromic acid (120 c.c., *d* 1·5), and glacial acetic acid (200 c.c.) were gently refluxed for 2 hours. The hydrobromic and acetic acids were removed under reduced pressure and the residue was dissolved in sodium hydroxide solution, filtered from traces of impurity, and the naphthol recovered. It boiled at

178—180°/15 mm. and crystallised from aqueous acetic acid in colourless needles (61 g.), m. p. 70—71° (Found : C, 83·2; H, 6·4. Calc. for $C_{11}H_{10}O$: C, 83·5; H, 6·3%).

7-*Amino*-1-*methylnaphthalene*.—The above naphthol (80 g.), ammonium sulphite (150 g.), concentrated aqueous ammonia (150 c.c.), and water (30 c.c.) were stirred in an autoclave at 160—170° for 8 hours. The product was extracted with benzene, washed with sodium hydroxide solution, and distilled. The fraction, b. p. 180—185°/15 mm., crystallised from methyl alcohol in colourless needles (60 g.), m. p. 85—86° (Found : N, 9·0. Calc. for $C_{11}H_{11}N$: N, 8·9%).

7-*Cyano*-1-*methylnaphthalene*.—A hot solution of 7-amino-1-methylnaphthalene (5 g.) in concentrated hydrochloric acid (7·5 c.c.) and water (20 c.c.) was cooled to − 10° (the hydrochloride separated) and diazotised with sodium nitrite (3·5 g.) in water (20 c.c.). The ice-cold diazo-solution was introduced into a warm solution of copper sulphate crystals (11·5 g.) and potassium cyanide (15 g.) in water (100 c.c.). The nitrile was distilled in steam, isolated with ether, and crystallised from light petroleum (b. p. 60—80°); colourless needles (1 g.), m. p. 71—72°, were obtained (Found : N, 8·6. $C_{12}H_9N$ requires N, 8·4%).

8-*Methyl*-2-*naphthyl Methyl Ketone*.—A solution of methylmagnesium iodide (from magnesium, 0·7 g., and methyl iodide, 4·3 g.) in ether (20 c.c.) was added to a solution of the above nitrile (3·3 g.) in toluene (30 c.c.). The ether was removed and the residual toluene suspension was gently refluxed for 1½ hours. Dilute sulphuric acid was added, and the toluene removed in steam; the product, isolated with ether, was a yellow oil (3 g.), b. p. 175—180°/15 mm., which slowly solidified. 8-*Methyl*-2-*naphthyl bromomethyl ketone*, obtained in 80% yield by the action of bromine on a chloroform solution of the above ketone, crystallised from benzene–light petroleum (b. p. 60—80°) in colourless prisms, m. p. 99—100° (Found : Br, 30·2. $C_{13}H_{11}OBr$ requires Br, 30·4%).

β-(8-*Methyl*-2-*naphthoyl*)*propionic Acid* (I).—The above bromo-derivative (8·3 g.) in benzene (30 c.c.) was gradually added to a suspension of ethyl sodiomalonate (prepared from sodium, 1·5 g., and ethyl malonate, 11 g.) in benzene (50 c.c.). After boiling for 12 hours, the mixture was diluted with water, the benzene layer separated, and the solvent removed. The residue was hydrolysed with methyl-alcoholic potassium hydroxide, and the malonic acid derivative was decarboxylated by heating at 180° for 3 hours. The product was esterified with methyl-alcoholic hydrogen chloride; the *methyl* ester of (I), b. p. 185—190°/0·5 mm., crystallised from methyl alcohol in colourless prisms, m. p. 87—88° (Found : C, 74·9; H, 6·4. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·2%). Hydrolysis with methyl-alcoholic potassium hydroxide yielded the *acid* (I), which crystallised from benzene in colourless prisms, m. p. 113—115° (Found : equiv., 244. $C_{15}H_{14}O_3$ requires equiv., 242).

γ-(8-Methyl-2-naphthyl)butyric acid, prepared by reduction of the above keto-acid (I) with amalgamated zinc and hydrochloric acid, was an oil. The *methyl* ester, was obtained as an oil, b. p. 170—175°/0·3 mm. (Found : C, 79·0; H, 7·2. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·4%).

1-*Keto*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydroanthracene* (II).—The butyric acid derivative (2·7 g.; obtained by hydrolysis of the above methyl ester) and thionyl chloride (2 c.c.) were heated for 2 hours, the excess of thionyl chloride removed, the residue dissolved in tetrachloroethane (20 c.c.), and aluminium chloride (3 g.) gradually introduced. After 12 hours, dilute hydrochloric acid was added, the tetrachloroethane removed in steam, and the residue extracted with ether. The extract was washed with dilute sodium hydroxide solution, the solvent removed, and the residue distilled. The fraction (0·4 g.), b. p. 180—190°/0·5 mm., was a slightly turbid, pale yellow oil, which did not crystallise and good analytical figures were not obtained (Found : C, 84·8; H, 6·5. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%).

1 : 5-*Dimethylanthracene*.—The ketotetrahydroanthracene (0·3 g.) was treated with methylmagnesium iodide (1 mol.) in ethereal solution. The mixture was decomposed with dilute sulphuric acid, and the product, after dehydration by heating with 98% formic acid (1 c.c.) for 1 hour, was heated with selenium (0·5 g.) at 280—300° for 24 hours. The product, isolated with chloroform, was distilled at 0·5 mm.; the distillate solidified and after three crystallisations from alcohol, 1 : 5-*dimethylanthracene* was obtained in pale yellow plates, m. p. 139—140° (Found : C, 93·2; H, 6·9. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%). The *picrate* crystallised from alcohol in scarlet needles, m. p. 166—167° (Found : C, 60·6; H, 4·0. $C_{22}H_{17}O_7N_3$ requires C, 60·7; H, 3·9%), and the *quinone* crystallised from acetic acid in very pale yellow, slender needles, m. p. 190° (Found : C, 81·1; H, 5·0. $C_{16}H_{12}O_2$ requires C, 81·4; H, 5·1%).

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE.

[*Received, October 2nd,* 1934.]