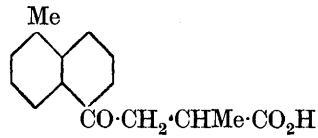
408. *Synthesis of Alkylphenanthrenes. Part V. 9-Methyl-, 1 : 9-Dimethyl-, and 1 : 2 : 8-Trimethylphenanthrenes.*

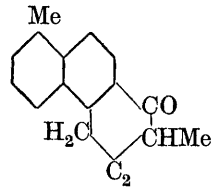
By R. D. Haworth and C. R. Mavin.

1-Methylnaphthalene reacted in nitrobenzene solution in the presence of aluminium chloride with acetyl chloride and succinic anhydride to yield 4-methyl-1-naphthyl methyl ketone and β-(4-*methyl*-1-*naphthoyl*)*propionic acid* respectively. These substances, unlike similar substances described in earlier parts of this series, on fusion with potassium hydroxide, underwent fission between the ketonic group and the naphthalene nucleus, but their conversion into 4-methyl-1-naphthoic acid on boiling with sodium hypochlorite solution established their constitutions. β-(4-Methyl-1-naphthoyl)-propionic acid was unusually resistant to reduction by Clemmensen's method, but the *methyl* ester was readily reduced and hydrolysed in this way. The reduction product was converted into 9-methylphenanthrene and 1 : 9-*dimethylphenanthrene* by methods developed for similar cases in previous communications in this series.

The primary object of this work was to prepare derivatives of 1-methylnaphthalene with a normal chain of four carbon atoms attached to the unsubstituted nucleus, and to utilise these substances for the synthesis of alkylphenanthrenes. Preliminary attempts to condense 4-bromo-1-methylnaphthalene with succinic anhydride were unpromising and finally 5-amino-1-methylnaphthalene was prepared by a slight modification of the method employed by Veselý, Štursa, Olejníček, and Rein (*Coll. Czech. Chem. Comm.*, 1929, **1**, 493). This amine was converted by the Sandmeyer reaction

into *5-cyano-1-methylnaphthalene*, which reacted with methylmagnesium iodide in boiling toluene solution to yield *5-methyl-1-naphthyl methyl ketone*. The oily ω-bromo-derivative of this ketone condensed with ethyl sodiomethylmalonate, and the product, after hydrolysis and heating at 160°, yielded β-(*5-methyl-1-naphthoyl*)*isobutyric acid* (I). The acid (I) was reduced and converted into *1-keto-*

(I.) 



(II.)

2 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (II), which was condensed with methylmagnesium iodide in ethereal solution, and the resultant carbinol converted into 1 : 2 : 8-trimethylphenanthrene by heating with selenium. The properties of this hydrocarbon, its picrate, quinone, and quinoxaline correspond with those recorded for the methylpimanthrene and its derivatives which Ruzicka and Hosking (*Helv. Chim. Acta*, 1931, **14**, 203) obtained from *iso*agathic dicarboxylic acid, and the constitution suggested by these authors is therefore confirmed.

Experimental.

β-(4-Methyl-1-naphthoyl)propionic acid, obtained in 80% yield from 1-methylnaphthalene and succinic anhydride, crystallised from MeOH or AcOH in long needles, m. p. 168—169° (Found: equiv., 239. $C_{15}H_{14}O_3$ requires equiv., 242). The *semicarbazone* crystallised from 70% AcOH in colourless needles, m. p. 202—203° (Found: N, 13·6. $C_{16}H_{17}O_3N_3$ requires N, 14·0%). The *methyl* ester, b. p. 196—198°/0·2 mm., crystallised from MeOH in stout prisms, m. p. 45—47° (Found: C, 75·3; H, 6·2. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%). The keto-acid (1 g.) was boiled for ½ hr. with 10% NaOH aq. (100 c.c.) containing Cl (from 2·1 g. $KMnO_4$ and 15 c.c. conc. HCl), the filtered solution saturated with SO_2, and the solid collected and crystallised from AcOH. Needles, m. p. 175—176°, were obtained, which gave no depression in m. p. with 4-methyl-1-naphthoic acid prepared by Mayer and Sieglitz's method (*Ber.*, 1922, **55**, 1839).

1-Keto-9-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene.—The methyl ester (5·1 g.) of the above keto-acid was reduced by Clemmensen's method, and the product (4 g.) cyclised in the usual manner. The cyclic ketone (2·4 g.) was purified by distillation at 0·2 mm. and crystallised from light petroleum (b. p. 60—80°) in stout prisms, m. p. 74—75° (Found: C, 85·5; H, 6·9. $C_{15}H_{14}O$ requires C, 85·6; H, 6·7%). The *semicarbazone* crystallised from 75% AcOH in slender prisms, m. p. 255—257° (Found: N, 15·6. $C_{16}H_{17}ON_3$ requires N, 15·7%).

9-Methylphenanthrene, obtained in 40% yield from the cyclic ketone on reduction by Clemmensen's method and dehydrogenation of the product with Se at 290—300°, crystallised from EtOH in stout prisms, m. p. 90—91°

(Found: C, 93·6; H, 6·3. Calc.: C, 93·7; H, 6·3%). The picrate crystallised from MeOH in orange needles, m. p. 153° (Found: N, 10·1. Calc.: N, 10·0%). Windaus, Jensen, and Schramme (*Ber.*, 1924, **57**, 1877) give 90—91° and 153° respectively.

1 : 9-*Dimethylphenanthrene*, obtained in 50% yield by dehydrogenating the product of the action of MgMeI on the cyclic ketone, crystallised from EtOH in slender prisms, m. p. 87—88° (Found: C, 93·1; H, 6·9. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%). The *picrate* crystallised from MeOH in orange-red needles, m. p. 160° (Found: N, 9·6. $C_{22}H_{17}O_7N_3$ requires N, 9·7%).

4-*Methyl*-1-*naphthyl Methyl Ketone*.—AcCl (7 c.c.) was gradually added with cooling to a solution of 1-methylnaphthalene (10 g.) and $AlCl_3$ (19 g.) in $PhNO_2$ (75 c.c.). After 24 hr., dil. HCl was added, the $PhNO_2$ removed in steam, and the residue extracted with C_6H_6, dried, and fractionated. The fraction (11·2 g.), b. p. 175—180°/15 mm., was treated with picric acid (15 g.) in MeOH, and after several crystns. the *picrate* (15·2 g.) was obtained in small yellow needles, m. p. 101—102° (Found: N, 10·3. $C_{19}H_{15}O_8N_3$ requires N, 10·2%). The ketone, regenerated from the picrate by the action of warm NH_3 aq., was an oil, b. p. 174—175°/15 mm., which gave an oily ω-bromo-derivative.

5-*Amino*-1-*methylnaphthalene*.—This was prepared essentially by Veselý, Šturša, Olejniček, and Rein's method (*loc. cit.*), but the desulphonation was modified. 4% Na amalgam (188 g.) was added to a solution of 5-amino-1-methylnaphthalene-4-sulphonic acid (25 g.) in *N*-NaOH (425 c.c.) and H_2O (575 c.c.) and after 1 hr.'s heating on the water-bath the base was distilled in steam, extracted with C_6H_6, dried, and the hydrochloride (17·9 g.) pptd. by HCl.

5-*Cyano*-1-*methylnaphthalene*.—5-Amino-1-methylnaphthalene hydrochloride (5 g.) in suspension in H_2O (100 c.c.) and conc. HCl (7·5 c.c.) was diazotised at − 5° ($NaNO_2$, 3·5 g.; H_2O, 20 c.c.), the solution run into warm CuCN ($CuSO_4$,$5H_2O$, 11·5 g.; KCN, 15 g.; H_2O, 100 c.c.), and the mixture distilled in steam for 6 hr.* From the distillate, Et_2O extracted 5-*cyano*-1-*methylnaphthalene*, which crystallised from light petroleum (b. p. 60—80°) in colourless prisms (1·5 g.), m. p. 92—93° (Found: N, 8·6. $C_{12}H_9N$ requires N, 8·4%).

5-*Methyl*-1-*naphthyl Methyl Ketone*.—The above nitrile (3·3 g.) in C_7H_8 (40 c.c.) was treated with MgMeI (Mg, 0·75 g.; MeI, 2 c.c.; Et_2O, 20 c.c.), the ether removed on the water-bath, and the residue boiled gently for 3 hr. Dil. H_2SO_4 was added, the C_7H_8 layer dried, the solvent removed through a column, and the residue distilled under reduced press. The *ketone* (2·5 g.), b. p. 182—184/19 mm., crystallised from light petroleum (b. p. 40—60°) in colourless plates, m. p. 44—46° (Found: C, 84·7; H, 6·6. $C_{13}H_{12}O$ requires C, 84·8; H, 6·5%).

β-(5-*Methyl*-1-*naphthoyl*)iso*butyric Acid* (I).—A solution of Br (1·5 c.c.) in CCl_4 (10 c.c.) was added with cooling to the above ketone (5 g.) dissolved in CCl_4 (15 c.c.). After 12 hr., HBr was removed in a stream of dry air, and the CCl_4 under diminished press. The oily residue, which did not crystallise from C_6H_6, Et_2O, or light petroleum, was added to ethyl sodiomethylmalonate (ethyl methylmalonate, 7·2 g.; "molecular" Na, 1 g.; C_6H_6, 70 c.c.), and the mixture refluxed for 12 hr. After addition of dil. HCl, the C_6H_6 layer was

* At this stage the distillation flask contained a black tar which slowly yielded nitrile on prolonged distillation. Superheated steam at 140° did not hasten the distillation appreciably.

separated, the solvent removed, the residue hydrolysed with warm methyl-alc. KOH, diluted with H_2O, and MeOH removed. Non-acidic impurities were removed in Et_2O, the alkaline layer was acidified, and the malonic acid derivative, isolated in Et_2O, was heated at 160° for 2 hr. The crude keto-acid (I) was boiled with methyl-alc. HCl for 2 hr., and the methyl ester, isolated in Et_2O, distilled. The fraction (3·2 g.), b. p. 196—199°/0·2 mm., hydrolysed with methyl-alc. KOH, yielded the *keto-acid* (I), which, cryst. from AcOH and then from MeOH, was obtained in colourless rectangular plates, m. p. 160—161° (Found: equiv., 254. $C_{16}H_{16}O_3$ requires equiv., 256).

1-*Keto*-2 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (II), prepared in 55% yield by reduction of the above keto-acid by Clemmensen's method and cyclisation of the product in the usual way, was purified by distillation at 0·2 mm. and crystn. from light petroleum (b. p. 60—80°), giving colourless plates, m. p. 108—109° (Found: C, 85·4; H, 7·3. $C_{16}H_{16}O$ requires C, 85·7; H, 7·1%). The *semicarbazone* crystallised from EtOH in colourless nodules, m. p. 256—258° (decomp.) (Found: N, 15·1. $C_{17}H_{19}ON_3$ requires N, 14·9%).

1 : 2 : 8-Trimethylphenanthrene, prepared in 60% yield by condensing the ketone (II) with MgMeI in Et_2O and heating the product with Se at 300—320° for 24 hr., crystallised from EtOH in plates, m. p. 144—145° (Found: C, 92·7; H, 7·3. Calc.: C, 92·7; H, 7·3%). The picrate crystallised from EtOH in long slender orange-red needles, m. p. 163° (Found: N, 9·4. Calc.: N, 9·3%), the quinone from EtOH or better from AcOH in slender orange prisms, m. p. 196—197° (Found: C, 81·5; H, 5·8. Calc.: C, 81·6; H, 5·6%), and the quinoxaline from EtOH–$CHCl_3$ or AcOH in very pale yellow needles, m. p. 131—132° (Found: N, 8·8. Calc.: N, 8·7%). Ruzicka and Hosking (*loc. cit.*) give 142—143°, 161—163°, 194°, and 131—132° as m. p.'s of methyl-pimanthrene, its picrate, quinone, and quinoxaline respectively.

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