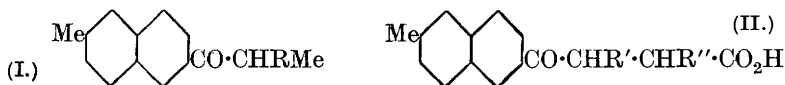


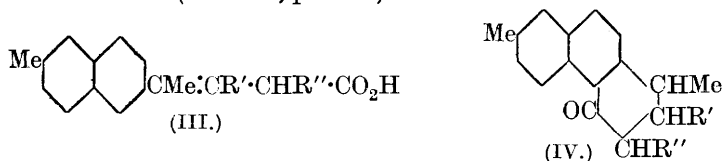
317. Synthesis of Alkylphenanthrenes. Part III.
 1 : 2 : 7-, 1 : 3 : 7-, and 1 : 6 : 7-Trimethylphenanthrenes.

By R. D. HAWORTH and (in part) F. M. BOLAM.

2-METHYLNAPHTHALENE and propionyl chloride reacted in the presence of aluminium chloride to yield 6-methyl-2-naphthyl ethyl ketone (I; R = H), the constitution of which was established by conversion into 6-methyl-2-naphthoic acid by fusion with potassium hydroxide. The ketone (I; R = H) was brominated, and the resultant 6-methyl-2-naphthyl α -bromoethyl ketone (I; R = Br) condensed with ethyl sodiomalonate; the product, after hydrolysis and heating at 160°, yielded β -(6-methyl-2-naphthoyl)butyric acid (II; R' = Me, R'' = H). The methyl ester of this acid was converted by way of γ -(6-methyl-2-naphthyl)- β -methyl- Δ^{β} -pentenoic acid (III; R' = Me, R'' = H) and 4-keto-1 : 2 : 7-trimethyl-



1 : 2 : 3 : 4-tetrahydrophenanthrene (IV; R' = Me, R'' = H) into 1 : 2 : 7-trimethylphenanthrene, by methods developed for similar cases in Part II (this vol., p. 1784).



In the synthesis of 1 : 3 : 7-trimethylphenanthrene, 2-methylnaphthalene was condensed with methylsuccinic anhydride to give β -(6-methyl-2-naphthoyl)isobutyric acid (II; R' = H, R'' = Me), which yielded 6-methyl-2-naphthoic acid on fusion with potassium hydroxide, and this together with the fact that it is not identical with the isomeric butyric acid derivative establishes the structure assigned to the acid. γ -(6-Methyl-2-naphthyl)- α -methyl- Δ^{β} -pentenoic acid (III; R' = H, R'' = Me), 4-keto-1 : 3 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (IV; R' = H, R'' = Me), and 1 : 3 : 7-trimethylphenanthrene were prepared by the usual methods.

2 : 3-Dimethylnaphthalene and succinic anhydride reacted to give β -(6 : 7-dimethyl-2-naphthoyl)propionic acid, which was converted into 6 : 7-dimethyl-2-naphthoic acid on fusion with potassium hydroxide. As the latter acid was also obtained by hydrolysis of 2-cyano-

6 : 7-dimethylnaphthalene, which resulted from the action of potassium cyanide on sodium 6 : 7-dimethylnaphthalene-2-sulphonate (Kruber, *Ber.*, 1929, 62, 3044) the structure assigned to the keto-acid is established. By an application of the usual methods γ -(6 : 7-dimethyl-2-naphthyl)- Δ^{β} -pentenoic acid, 4-keto-1 : 6 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, and 1 : 6 : 7-trimethylphenanthrene were prepared.

The constants for the synthetical trimethylphenanthrenes and their derivatives do not correspond with those recorded for the methylpimanthrenes obtained from *d*-pimaric and *isoagathic* dicarboxylic acids.

The structure assigned to pimanthrene establishes the 1 : 7-positions of the two methyl groups of *d*-pimaric acid, and the synthesis of the trimethylphenanthrenes described in this and earlier communications proves that the carboxyl group cannot be situated in the 2-, 3-, 4-, or 6-position.

EXPERIMENTAL.

6-Methyl-2-naphthyl Ethyl Ketone (I; R = H).—Propionyl chloride (15 g.) was gradually added with cooling to a solution of 2-methylnaphthalene (23 g.) and AlCl₃ (44 g.) in PhNO₂ (100 c.c.). After 48 hrs., dil. HCl was added, the PhNO₂ removed in steam, and the residue extracted with C₆H₆, dried, and fractionated. The ketone (I; R = H; 20 g.), b. p. 198—200°/15 mm., crystallised from light petroleum (b. p. 40—60°) in colourless needles, m. p. 61—62° (Found : C, 84.4; H, 7.1. C₁₄H₁₄O requires C, 84.8; H, 7.1%). The ketone (0.5 g.) and KOH (2.5 g.) were fused at 250° for 15 mins.; 6-methyl-2-naphthoic acid, m. p. 225—226°, was obtained and identified by comparison with a specimen prepared from β -(6-methyl-2-naphthoyl)propionic acid and also by conversion into the methyl ester, m. p. 116—117°.

6-Methyl-2-naphthyl α -bromoethyl ketone (I; R = Br), obtained by adding Br (1.1 c.c.) with cooling to the above ketone (3.4 g.) in CCl₄ (20 c.c.), after 3 hrs. removing the HBr in a current of air and the solvent under reduced press., crystallised from light petroleum (b. p. 60—80°) in prisms, m. p. 92—93° (Found : C, 60.9; H, 4.7. C₁₄H₁₃OBr requires C, 60.6; H, 4.7%).

β -(6-Methyl-2-naphthoyl)butyric Acid (II; R' = Me, R'' = H).—The above bromide (15 g.) and ethyl sodiomalonate (Na, 1.9 g.; ethyl malonate, 13 g.) were heated for 12 hrs. in C₆H₆ solution, the mixture acidified, the C₆H₆ layer separated, the solvent removed, and the residual oil hydrolysed with methylal. KOH. The dicarboxylic acid, isolated with Et₂O, was heated at 160—170° for 2 hrs., and the residue crystallised from C₆H₆; needles (6.2 g.), m. p. 118—120° (Found : C, 74.8; H, 6.1. C₁₆H₁₆O₃ requires C, 75.0; H, 6.3%). The methyl ester was an oil, b. p. 195—198°/0.2 mm.

4-Keto-1 : 2 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (IV; R' = Me, R'' = H).—The above ester (8 g.) was treated with MgMeI (MeI, 6.3 g.; Mg, 1.1 g.), the mixture decomposed with dil. H₂SO₄, and the ethereal layer extracted with Na₂CO₃ aq. The crude pentenoic acid (III; R' = Me, R'' = H), obtained as an oil (6 g.), was reduced with P and HI. The resultant semi-solid acid (4 g.) was converted in 70% yield into the cyclic ketone (IV; R' = Me,

R'' = H) by the action of H_2SO_4 . The ketone was an oil, b. p. 195—198°/0.5 mm., yielding a *semicarbazone* which separated from EtOH in stout prisms, m. p. 217—218° (decomp.) (Found: C, 73.1; H, 7.1. $C_{18}H_{21}ON_3$ requires C, 73.2; H, 7.1%).

1 : 2 : 7-*Trimethylphenanthrene*.—The cyclic ketone was reduced by Clemmensen's method, and the product dehydrogenated with Se. 1 : 2 : 7-*Trimethylphenanthrene* crystallised from EtOH in colourless plates, m. p. 120—121° (Found: C, 92.6; H, 7.2. $C_{17}H_{16}$ requires C, 92.7; H, 7.3%), the *picrate* in orange needles, m. p. 148—149° (Found: N, 9.5. $C_{23}H_{19}O_7N_3$ requires N, 9.3%), the *stypnate* in orange needles, m. p. 169—170° (Found: C, 59.1; H, 4.1. $C_{23}H_{19}O_8N_3$ requires C, 59.4; H, 4.1%), the *quinone* in orange plates, m. p. 209—210° (Found: C, 81.3; H, 5.7. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.6%), and the *quinoxaline* from AcOH in cream-coloured needles, m. p. 184—185° (Found: N, 8.9. $C_{23}H_{18}N_4$ requires N, 8.7%).

β -(6-*Methyl-2-naphthoyl*)isobutyric acid (II; R' = H, R'' = Me) was prepared in 60% yield from 2-methylnaphthalene and methylsuccinic anhydride; colourless plates, m. p. 182—183°, from AcOH or MeOH (Found: equiv., 254. $C_{16}H_{16}O_3$ requires equiv., 256). The *methyl ester*, b. p. 230—240°/15 mm., crystallised from MeOH in needles, m. p. 88—89° (Found: C, 75.3; H, 6.8. $C_{17}H_{18}O_3$ requires C, 75.6; H, 6.7%).

γ -(6-*Methyl-2-naphthyl*)- α -methyl- Δ^{β} -pentenoic acid (III; R' = H, R'' = Me) obtained by the action of MgMeI on the above ester, crystallised from MeOH in needles, m. p. 150—151° (Found: C, 79.9; H, 7.3. $C_{17}H_{18}O_2$ requires C, 80.3; H, 7.1%).

4-*Keto-1 : 3 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene* (IV; R' = H, R'' = Me) was an oil, b. p. 190—195°/0.4 mm. (Found: C, 85.5; H, 7.6. $C_{17}H_{18}O$ requires C, 85.7; H, 7.5%).

1 : 3 : 7-*Trimethylphenanthrene* crystallised from MeOH in colourless prisms, m. p. 68—69° (Found: C, 92.4; H, 7.2%), the *picrate* from EtOH in pale orange needles, m. p. 163—164° (Found: C, 61.5; H, 4.1. $C_{23}H_{19}O_7N_3$ requires C, 61.5; H, 4.3%), the *stypnate* in yellow tufted needles, m. p. 160—161°, the *quinone* in slender orange needles, m. p. 174—175° (Found: C, 81.4; H, 5.7%), and the *quinoxaline* from AcOH in slender cream needles, m. p. 201—202° (Found: N, 8.9%).

β -(6 : 7-*Dimethyl-2-naphthoyl*)propionic acid, obtained in 70% yield from 2 : 3-dimethylnaphthalene and succinic anhydride, crystallised from AcOH or MeOH in colourless plates, m. p. 179—180° (Found: equiv., 255. $C_{16}H_{16}O_3$ requires equiv., 256). The *methyl ester*, b. p. 235—240°/12 mm., separated from MeOH in needles, m. p. 95—96° (Found: C, 75.4; H, 6.5%).

6 : 7-*Dimethyl-2-naphthoic Acid*.—(a) Pure 2 : 3-dimethylnaphthalene (20 g.) and conc. H_2SO_4 (15 c.c.) were heated for 2 hrs. at 100°; the mixture was diluted with H_2O and neutralised with NaOH aq., and the sparingly sol. sodium 6 : 7-dimethylnaphthalene-2-sulphonate crystallised from H_2O (yield, 32 g.). The Na salt (35 g., dried at 120°) and KCN (25 g.) were heated in a metal retort, the sublimate was dissolved in $CHCl_3$, washed with H_2O and then with dil. NaOH aq., and dried, and the solvent removed. The residue (10 g.), consisting of a mixture of 2-cyano-6 : 7-dimethylnaphthalene and 2 : 3-dimethylnaphthalene, was heated with AcOH (40 c.c.), conc. H_2SO_4 (30 c.c.), and H_2O (30 c.c.) for 12 hrs. The mixture was diluted and extracted with Et_2O , and the acid removed in NaOH aq., recovered, and isolated with Et_2O . (b) β -(6 : 7-*Dimethyl-2-naphthoyl*)propionic acid (1 g.) and KOH (5 g.) were fused at 250°

for 20 mins., the melt diluted and acidified, and the acid isolated with Et_2O . 6 : 7-Dimethyl-2-naphthoic acid, obtained by either method (a) or (b), was crystallised from a little MeOH and then from C_6H_6 -EtOH; colourless plates, m. p. 254—255° (Found: equiv., 198. $\text{C}_{13}\text{H}_{12}\text{O}_2$ requires equiv., 200). The methyl ester, prepared from CH_2N_2 and the acid in Et_2O , crystallised from MeOH in rosettes of needles, m. p. 147—148° (Found: C, 78.1; H, 6.4. $\text{C}_{14}\text{H}_{14}\text{O}_2$ requires C, 78.5; H, 6.6%).

γ -(6 : 7-Dimethyl-2-naphthyl)- Δ^{β} -pentenoic acid crystallised from MeOH in plates, m. p. 155—156° (Found: C, 79.9; H, 7.0%).

4-Keto-1 : 6 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene was an oil, b. p. 190—192°/0.4 mm., yielding a semicarbazone, which crystallised from EtOH in jagged prisms, m. p. 200—202° (Found: N, 14.0. $\text{C}_{18}\text{H}_{21}\text{ON}_3$ requires N, 14.2%).

1 : 6 : 7-Trimethylphenanthrene crystallised from EtOH in colourless plates, m. p. 123—124° (Found: C, 92.8; H, 7.3%), the picrate in orange needles, m. p. 165—166° (Found: C, 61.2; H, 4.5%), the styphnate in feathery yellow needles, m. p. 111—112°, the quinone from AcOH in orange rhombic prisms, m. p. 221—222° (Found: C, 81.3; H, 5.7%), and the quinoxaline in buff-coloured needles, m. p. 189—190° (Found: N, 8.6%).

Our thanks are due to Mr. C. R. S. Tenniswood, M.Sc., for most of the analytical results.

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[Received, July 2nd, 1932.]
