CCCXIII.—*A Synthesis of 4-Methylphenanthrene.*

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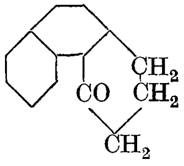
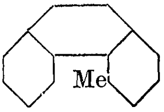
Podocarpic acid, $C_{17}H_{22}O_3$, was first isolated by Oudemans (*Ber.*, 1873, **6**, 1122, 1125; *Annalen*, 1873, **170**, 214) from the resin of a Javanese podocarp, and was subsequently obtained by Easterfield and Aston (*Trans. New Zealand Inst.*, 1904, **36**, 483; 1911, **43**, 53; P., 1903, **19**, 190) from the resin which occurs in shakes in the wood of *Dacrydium cupressinum* (" rimu ") and of *Podocarpus dacrydioides* (" kahikatea "). By distilling the pure acid with zinc dust, Oudemans obtained a hydrocarbon, $C_{15}H_{12}$, which he believed to be a methylanthracene and therefore assigned to it the name methanthrene; Easterfield and Bagley (J., 1904, **85**, 1242), however, suggested that it might be a methylphenanthrene.

We have obtained the same hydrocarbon both by Oudemans's method and, in better yield, by selenium dehydrogenation of podocarpic acid. The quinone, $C_{15}H_{10}O_2$, produced by the oxidation of methanthrene readily yields a *quinoxaline*, thus indicating that the hydrocarbon is a derivative of phenanthrene, and a survey of the literature led to the conclusion that it is probably 4-*methylphenanthrene*. We therefore decided to synthesise this hydrocarbon. We first attempted to apply the well-known Pschorr synthesis, but, being unable to transform the resulting carboxylic acid into 4-methylphenanthrene, we resorted to a method based on that employed by Ruzicka and Seidel (*Helv. Chim. Acta*, 1922, **5**, 369) in the synthesis of cadalene. The yield obtained by the condensation of α-naphthyl methyl ketone with bromoacetic ester according to the Reformatsky method, however, was unsatisfactory. In a further attempt we condensed 1-α-chloroethylnaphthalene with ethyl sodiomalonate and obtained β-1-naphthylbutyric acid, $C_{10}H_7{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$ (m. p. 108°), in good yield. Difficulties were, however, encountered in attempting the reduction of the corresponding ester by the Bouveault–Blanc method, the nucleus being attacked as well as the side chain under all the conditions tried. The acid has subsequently been degraded by the Curtius–Schroeter method and we hope to obtain both 4-methylphenanthrene and 1 : 4-dimethylphenanthrene by this route.

Finally, we prepared 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (I), essentially according to the method of Schroeter, Müller, and Huang (*Ber.*, 1929, **62**, 657), and condensed it with methylmagnesium iodide. The resulting carbinol lost water on distillation, and dehydrogenation of the product with selenium gave 4-methylphenanthrene (II) in satisfactory yield. A careful comparison disclosed no differences between the synthetic hydrocarbon and that obtained from podocarpic acid. The hydrocarbons, quinones, and quinoxalines melted at the same temperature, either alone or after admixture. The picrates and styphnates were also identical, but these are less satisfactory for purposes of comparison owing to their relative instability. The relation between 4-methylphenanthrene and podocarpic acid will be discussed in a subsequent communication.

(I.)





(II.)

EXPERIMENTAL.

Methanthrene from Podocarpic Acid.—(1) Podocarpic acid was distilled with zinc dust as described by Oudemans (*Annalen*, 1873, **170**, 243), and the distillate was dissolved in ether, extracted with 10% sodium hydroxide solution, and distilled at 2 mm. Fraction (i), b. p. <155°, was a light yellow oil; fraction (ii), b. p. 155—185°, solidified on cooling; and fraction (iii), b. p. 185—205°, was a viscous brown oil which deposited a small quantity of solid on cooling. The united solids, after recrystallisation from 95% alcohol to remove an impurity which turns black on exposure to air, melted at about 112°. Sublimation and recrystallisation from alcohol finally produced colourless crystals, m. p. 117° (Found: C, 93·7, 93·5;

H, 6·3, 6·5. Calc. for $C_{15}H_{12}$: C, 93·8; H, 6·2%). The average yield was 0·5% of the weight of the acid employed. The picrate, prepared from 19 mg. of hydrocarbon and 23 mg. of picric acid in 0·5 c.c. of absolute alcohol, formed brownish-red needles, m. p. 125·5° (Oudemans gives m. p. 117°). The styphnate, similarly obtained from 19 mg. of methanthrene and 24 mg. of styphnic acid, separated in small orange needles, m. p. 144·5°. Both derivatives were too unstable for satisfactory recrystallisation. The quinone was obtained by slowly adding a solution of chromic anhydride (0·45 g.) in water (0·5 c.c.) and acetic acid (2·4 c.c.) to a solution of the hydrocarbon (0·2 g.) in acetic acid (1 c.c.) at 50°, the reaction being completed by heating in steam for ½ hour. The crystals which separated on cooling were washed with ether and recrystallised from 70% alcohol. They formed orange-yellow plates, m. p. 187—187·5° (Oudemans gives m. p. 187°) (Found: C, 81·2, 81·3; H, 4·6, 4·8. Calc. for $C_{15}H_{10}O_2$: C, 81·1; H, 4·5%). The *quinoxaline* was prepared by heating together solutions of *o*-phenylenediamine (22 mg.) in absolute alcohol (0·5 c.c.) and of the quinone (32 mg.) in acetic acid (0·5 c.c.) on the steam-bath for 1½ hours. It separated from absolute alcohol–chloroform in cream-yellow, felted needles, m. p. 177° (Found: C, 85·7, 85·7; H, 4·9, 5·0; N, 9·4, 9·3. $C_{21}H_{14}N_2$ requires C, 85·7; H, 4·8; N, 9·5%).

(2) A mixture of podocarpic acid (20 g.) with powdered selenium (35 g.) was heated to 290°, and the temperature raised to 340° during 30 hours. The residue was powdered, extracted with ether in a Soxhlet apparatus, and the extract washed with 10% sodium hydroxide solution and with water. The solid residue (1·9 g.) after removal of the solvent from the dry solution furnished a slightly coloured solid (1 g.; b. p. 165—170°) when distilled at 2—2·5 mm.; a black resin remained. The distillate melted at 117° after repeated crystallisation from 95% alcohol. The picrate, styphnate, quinone, and quinoxaline were identical with those obtained by the previous method.

β-Naphthyl methyl ketone (m. p. 54°) was obtained in 48—50% yield by the condensation of β-naphthonitrile with methylmagnesium iodide (1·5 mols.) at the b. p. of toluene. No appreciable reaction occurs in ethereal solution. The α-ketone, b. p. 162·5—163·5°/12 mm. (picrate, m. p. 118°), was prepared in equal yield by the same method.

Bromomethyl β-*Naphthyl Ketone.*—A solution of bromine (10 g.) in carbon tetrachloride (30 g.) was slowly added (at room temperature) to β-naphthyl methyl ketone (10 g.) dissolved in the same solvent (30 g.). Hydrogen bromide was removed by aspirating dry air through the solution, and the solvent was then removed under diminished pressure, finally at 50—60°. The solid residue was recrystallised from ether–light petroleum (b. p. $<40°$), and yielded white needles, m. p. 80° (Found, by the Stepanov–Rosanoff method: Br, 32·3. Calc.: Br, 32·1%). The picrate, a buff-coloured microcrystalline powder, may be recrystallised from alcohol; it melts at 93°. Bromomethyl α-naphthyl ketone (b. p. 176—178°/3 mm.; $n_D^{20°}$ 1·6643. Found, by the Stepanov–Rosanoff method: Br, 32·6. Calc.: Br, 32·1%) was prepared from α-naphthyl methyl ketone in the same way. Its picrate consists of light yellow needles, m. p. 80·5°, sparingly soluble in alcohol.

4-*Keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene.*—Bromomethyl-β-naphthyl ketone was condensed with ethyl sodiomalonate (1 mol.) in benzene solution essentially according to the method of Schroeter, Müller, and Huang (*Ber.*, 1929, **62**, 657. Compare also Kroll-pfeiffer and Schafer, *Ber.*, 1923, **56**, 623; Schafer, Diss., Marburg, 1922). Considerably lower yields were obtained in alcoholic solution. The ethyl 2-naphthacylmalonate so obtained was converted into γ-2-naphthylbutyric acid as described by these authors, and we confirmed their results in all essential details. The transformation of this acid into 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene by the action of phosphorus pentachloride gave a much smaller yield than that recorded by Schroeter and his co-workers, but substitution of thionyl chloride (3 mols.) gave a much better yield. The ketone melted at 69°.

4-*Methylphenanthrene.*—The cyclic ketone (2·4 g.) was condensed with methylmagnesium iodide (1·5 mols.) in benzene–ether solution * (15 c.c.), the mixture being finally boiled for an hour. The product was decomposed with ice-cold, dilute sulphuric acid, taken up in ether, washed with dilute sodium hydroxide solution and with water, and dried over sodium sulphate. A semi-solid mass remained after removal of the solvent, and appeared to be a mixture of the tertiary alcohol with the hydrocarbon resulting from its dehydration. On distillation, a small quantity of water was evolved and the residual oil (2 g.) passed over at 170—175°/11 mm. Dehydrogenation was effected by heating a mixture of selenium powder (2·0 g.) with the hydrocarbon (1·8 g.) for 30 hours at 300—340°. The product was extracted with ether, and after removal of the solvent there remained a grey solid, which on distillation passed over at 175—185°/10 mm., leaving a small resinous residue. The distillate (1·05 g.) rapidly solidified on cooling, and after several recrystallisations from 95% alcohol, melted at 117° (Found: C,

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* When the condensation was conducted in toluene in absence of ether, the sole product of the synthesis was phenanthrene (quinone, m. p. 206°; quinoxaline, m. p. 224°).

93·5, 93·6; H, 6·5, 6·6. $C_{15}H_{12}$ requires C, 93·8; H, 6·2%). The picrate and styphnate melted at 125° and 144° respectively.

4-*Methylphenanthraquinone* was prepared from the synthetic hydrocarbon (0·2 g.) by the method already described and melted at 187—187·5° (Found: C, 81·4, 81·2; H, 4·9, 4·5. $C_{15}H_{10}O_2$ requires C, 81·1; H, 4·5%); it yielded the *quinoxaline*, m. p. 177° (Found: C, 85·6, 85·6; H, 4·8, 4·9; N, 9·2, 9·4. $C_{21}H_{14}N_2$ requires C, 85·7; H, 4·8; N, 9·5%), on condensation with *o*-phenylenediamine.

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