143. *Syntheses of Polycyclic Compounds Related to the Sterols. Part IV. The Identification of 3'-Methyl-1 : 2-*cyclo*pentenophenanthrene and its Preparation from Cholesterol.*

By D. J. C. GAMBLE, G. A. R. KON, and B. SAUNDERS.

IN Part II it was concluded, from a comparison of the hydrocarbon $C_{18}H_{16}$ (D) resulting from the dehydrogenation of sterols and bile acids (Diels, Gädke, and Körding, *Annalen*, 1927, **459**, 1) with 3'-methyl-1 : 2-*cyclo*pentenophenanthrene (K) prepared synthetically (Harper, Kon, and F. Ruzicka, J., 1934, 124), that these hydrocarbons are identical; this conclusion received strong support from the crystallographic examination of these compounds and of their derivatives by Bernal and Crowfoot (this vol., p. 93). Since then, Hillemann (*Ber.*, 1935, **68**, 102) has prepared from the hydrocarbon (B) synthesised by Bergmann and himself (*ibid.*, 1933, **66**, 1302) the nitroso-derivative already obtained by Diels *et al.* (*loc. cit.*) from D, whilst Diels and Rickert (*Ber.*, 1935, **68**, 267) have prepared the same tribromo-derivative from both D and K, thus further confirming their identity; and we have since obtained this compound from B.

It nevertheless appeared desirable to elucidate the nature of the small differences

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* Erdtman (*loc. cit.*) converted " sulphite-liquors lactone " dimethyl ether into the corresponding dibasic acid by the action of sodium hypobromite, and the difficulty now experienced is probably due to a steric effect introduced by the planar configuration of the lactone (XIX).

observed between the hydrocarbons of different origin, and also between their derivatives, bearing in mind their importance for the diagnosis of a sterol-like skeleton in many natural products.

When the hydrocarbon K was prepared with care to avoid overheating in the course of dehydrogenation, the product only differed from B in that its solutions had a strong blue fluorescence in daylight, and the picrate, although identical in appearance, melted at 127—128°; the other derivatives had identical properties :

	Hydrocarbon.	Trinitrobenzene compound.	Trinitrotoluene compound.	Styphnate.
M. p.	125—126°	148—149°	96—97°	135—136°

The hydrocarbon was then further purified by chromatographic adsorption, already successfully employed by Diels and Rickert (*loc. cit.*); the product no longer gave fluorescent solutions and in ultra-violet light the fluorescence was violet, not blue. The m. p. of the picrate was now 130—131°, or about 1° lower than that of the purest B, and was not altered by recrystallisation.

A hydrocarbon of identical properties has also been isolated by repeated purification, by the adsorption method, of a sample of D prepared from cholesterol; we wish to emphasise that this material also showed no fluorescence in daylight and exhibited a property commented on by Diels and Rickert (*loc. cit.*) as being characteristic of K, namely, that the crystals separating from an alcoholic solution lose their lustre when the solution attains room temperature.

The purest specimen of D gave a picrate, m. p. 127—128°, unaltered by repeated crystallisation, and the other derivatives had the properties already recorded for the corresponding derivatives of B and K.

It can therefore be concluded that substantially pure 3′-methyl*cyclo*pentenophenanthrene has been isolated from the dehydrogenation product of cholesterol. The varying melting points of the picrate are not due to a gross impurity, no trace of which could be revealed by analysis, but are probably attributable to the formation of variable quantities of the second form of the picrate, namely, the stable form, m. p. 117°, of Bernal and Crowfoot (*loc. cit.*).* It follows that the picrate has little diagnostic value for the identification of the hydrocarbon, but both the styphnate (Gamble and Kon, this vol., p. 443) and the *s*-trinitrobenzene compound are suitable; the trinitrotoluene compound is somewhat soluble and therefore not to be recommended for small-scale work. The purification of the tribromo-derivative also requires a fairly large amount of material, and the nitroso-derivative is altogether unsuitable.

EXPERIMENTAL.

Hydrocarbon K.—The preparation was carried out essentially as described by Harper, Kon, and Ruzicka (*loc. cit.*), but the use of naphthylethyl bromide in place of the chloride is advantageous. The nature of the magnesium is also important, the best result being obtained with a sample supplied by the Mallinckrodt Chemical Co. of Philadelphia; it is advisable to use a 50% excess of magnesium and to add the ketone very soon after all the bromide has been introduced.

In the dehydrogenation of the hydrocarbon $C_{19}H_{20}$ it is important not to exceed a bath temperature of 330°; the formation of the high-melting by-product is almost entirely prevented in this way. The hydrocarbon was distilled and converted into the picrate, m. p. 127—128° (constant) after two crystallisations from benzene–alcohol (1 : 5). The hydrocarbon was regenerated from the picrate and repeatedly crystallised from alcohol. A portion was reconverted into the picrate, and this repeatedly crystallised from alcohol–benzene, a product of m. p. 129—130° being obtained; the other derivatives prepared had the correct m. p.'s given above.

Finally, the hydrocarbon was subjected to chromatographic adsorption, following the method of Winterstein and Stein (*Z. physiol. Chem.*, 1933, **220**, 247) and Diels and Rickert (*loc. cit.*);

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* [Added in proof.] The authors are indebted to Miss D. Crowfoot for a crystallographic examination of the three hydrocarbons and their picrates. The hydrocarbons were indistinguishable, but the picrate of D differed from those of B and K in the much slower conversion of the metastable into the stable form, a result in agreement with the view expressed above.

it is advantageous to use rather more solvent than is recommended by the latter authors. 1·5 G. of the hydrocarbon in 150 c.c. of petroleum (b. p. 70—80°) were allowed to percolate through a column of about 100 g. of alumina contained in a tube 22 mm. wide; 300 c.c. of the same solvent were then used for "developing." After two treatments the hydrocarbon was recovered, recrystallised from alcohol, and used for the preparation of derivatives; the picrate, which formed fine orange-yellow needles, had m. p. 130—131°.

Hydrocarbon B.—The specimen was prepared as described by Bergmann and Hillemann (*loc. cit.*); it could not be satisfactorily purified by crystallisation and was therefore converted into the picrate; this was recrystallised, and the hydrocarbon regenerated from the pure compound, m. p. 131—132°. The specimen was then distilled under 0·2 mm. pressure, as recommended by Hillemann (*loc. cit.*), a colourless distillate being obtained. The compound, recrystallised from alcohol, formed plates, m. p. 125—126°; the needle-shaped form previously observed (Harper, Kon, and Ruzicka, *loc. cit.*) was not obtained. The hydrocarbon, though pure, has less tendency to form well-defined crystals than K. The picrate prepared from the pure hydrocarbon was exactly like that of K in appearance and had m. p. 131—132°.

Hydrocarbon D.—250 G. of dry cholesterol were dehydrogenated with 500 g. of selenium by heating for 3 hours at 280° and for 50 hours at 330—360° (Ruzicka, Goldberg, and Thomann, *Helv. Chim. Acta*, 1933, **16**, 812); 160 g. of oil were recovered and fractionated at 0·8—0·4 mm.: (1) below 115°, 2·0 g.; (2) 115—158°, 4·8 g.; (3) 158—190°, 45·0 g., solidified in part; (4) 190—213°, 37·5 g., solidified in part; (5) 213—245°, 47·2 g. of light brown oil; (6) 245—295°, 20·7 g. of dark brown gum. The last four fractions were refractionated, fractions being collected at 10° intervals. Four fractions collected below 190°, together with fraction (2) above, were each dissolved in benzene and treated with an equal weight of *s*-trinitrobenzene in hot alcohol–benzene. The trinitrobenzene compound formed was dissolved in cold *cyclo*hexane (which left behind the excess of trinitrobenzene), recovered by evaporation under reduced pressure, and fractionally crystallised from alcohol–benzene. Orange-yellow needles, m. p. 146—147°, were obtained after 10—15 crystallisations.

A further quantity of this material was derived from the fractions of b. p. 190—200° and 200—210°, which were redistilled over sodium, yielding a colourless oil. This solidified to a large extent; the solid was rubbed with cold pentane, filtered off, and treated with trinitrobenzene as above. The higher fractions of the oil did not react with trinitrobenzene.

The hydrocarbon recovered from the trinitrobenzene compound by means of stannous chloride was recrystallised from alcohol (charcoal) and formed indefinite, somewhat coloured plates, m. p. 126—129°; a pure individual compound could not be obtained from it by the usual methods.

The crude hydrocarbon (1·5 g.) was then treated with alumina as described above; a colourless, well-crystallised material was recovered after two treatments, but this still melted somewhat high and therefore the process was repeated twice more; 1·0 g. of hydrocarbon was obtained, m. p. 124—125° with previous sintering, 125—126° after three crystallisations from alcohol (Found: C, 92·8, 93·0; H, 6·9, 6·8. Calc.: C, 93·1; H, 6·9%). The picrate prepared from this was in every way similar to the picrate of K, but melted at 127—128° (Found: C, 62·5; H, 4·1. Calc.: C, 62·5; H, 4·1%); the other derivatives had the correct m. p.'s given on p. 645.

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IMPERIAL COLLEGE, LONDON, S.W. 7.

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