33. *Syntheses of Polycyclic Compounds Related to the Sterols. Part II. Diels's Hydrocarbon* $C_{18}H_{16}$.

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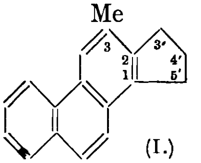
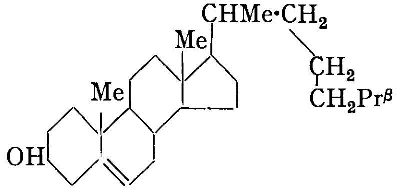
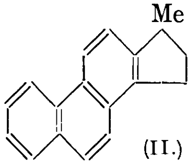
In Part I (J., 1933, 1084) it was pointed out that synthetic 1 : 2-*cyclo*pentenophenanthrene does not depress the melting point of Diels's hydrocarbon which results from the dehydrogenation of cholesterol and other cholane derivatives. The melting points of several of the derivatives, however, show considerable differences, and the crystallographic measurements of Bernal and Crowfoot (*Chem. and Ind.*, 1933, **52**, 729) finally establish that the two hydrocarbons cannot be identical. Of the methyl*cyclo*pentenophenanthrenes, the 4'- and the 5'-compound have been prepared by L. Ruzicka, Ehmann, Goldberg, and Hösli (*Helv. Chim. Acta*, 1933, **16**, 833) and found to differ from Diels's compound. The migration of the methyl group which is assumed to take place in the dehydrogenation of cholesterol could also lead to the 3- or the 3'-compound (I and II) :



(I.)





(II.)

Bergmann and Hillemann prepared the latter (*Ber.*, 1933, **66**, 1302), but were unable to settle the question of its identity. We have therefore repeated their preparation and, because of its laborious nature, have also devised a simpler method.

Before the appearance of Bergmann and Hillemann's paper we had attempted to obtain the desired compound by adapting the method of Bogert (*Science*, 1933, **77**, 289), subsequently used by Cook and Hewett (J., 1933, 1099)*; Bardhan and Sengupta's method (J., 1932, 2520), which was employed in Part I, although affording clear proof of the structure of the products, fails in the present instance because the initial material, ethyl 3-methyl*cyclo*pentanone-2-carboxylate, is not known.

2-Methyl*cyclo*pentanone reacted with β-(α-naphthyl)ethylmagnesium bromide, giving the *carbinol* (III), which was dehydrated with phosphoric oxide in the hope that cyclisation would yield the hydrocarbon (IV), from which (II) could be obtained on dehydrogenation. The hydrocarbon, however, yielded *cyclo*pentenophenanthrene, the formation of which supports the reaction mechanism, suggested by Bogert (*loc. cit.*), involving the intermediate formation of an unsaturated hydrocarbon (such a hydrocarbon was, in fact, described in Part I, *loc. cit.*). The elimination of water from the carbinol (III) would normally be expected

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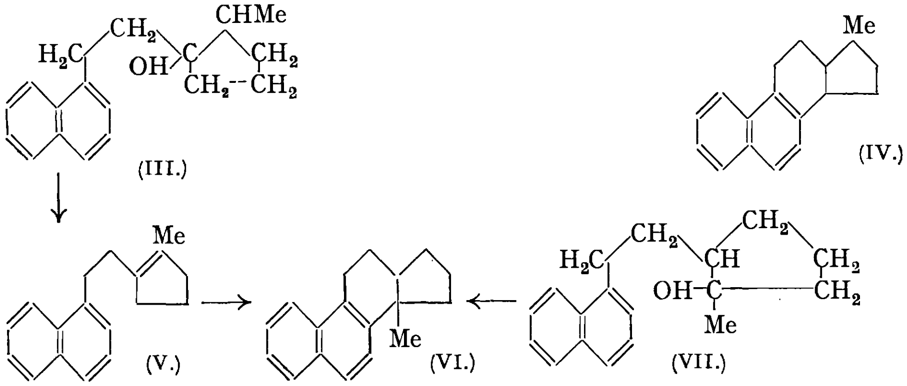
* The preparation of *cyclo*pentenophenanthrene as described below was completed during July, 1933, before the appearance of Cook and Hewett's paper.

to give the compound (V), and this can only cyclise to give (VI). The compound (VI) has also been obtained by the process described in Part I, namely, by the dehydration

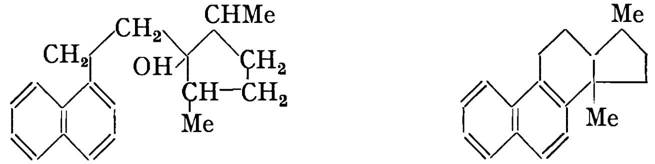


(III.) (IV.) (V.) (VI.) (VII.)

of the tertiary *alcohol* (VII) resulting from the action of methylmagnesium iodide on 2-β-(α-naphthyl)ethyl*cyclo*pentanone. The *hydrocarbon* (VI) readily loses the methyl group and gives *cyclo*pentenophenanthrene in good yield; the formation of the by-product, m. p. 182—183°, was not observed on this occasion.

To overcome this difficulty, 2 : 5-dimethyl*cyclo*pentanone was employed in the above reaction. The *alcohol* (VIII) was dehydrated to the *hydrocarbon* (IX), and this gave the required compound (II) on dehydrogenation.

(VIII.)



(IX.) ⟶ (II)

3′-*Methyl*-1 : 2-cyclo*pentenophenanthrene* and its *picrate*, *trinitrobenzene* compound, and *trinitrotoluene* compound are identical in appearance and m. p. with the corresponding compounds prepared from cholesterol; we are particularly indebted to Mr. J. D. Bernal for the loan of two specially purified samples of Diels's hydrocarbon, with which the comparison was carried out. The melting points of mixtures of the synthetic compounds with the relevant derivatives of Diels's hydrocarbon are identical with those of the pure compounds, but no great weight is attached to this observation because the method of mixed melting points is known to be unreliable in this series of compounds. As a matter of fact, the melting points of our new compounds are not depressed in admixture with the appropriate compounds of *cyclo*pentenophenanthrene.

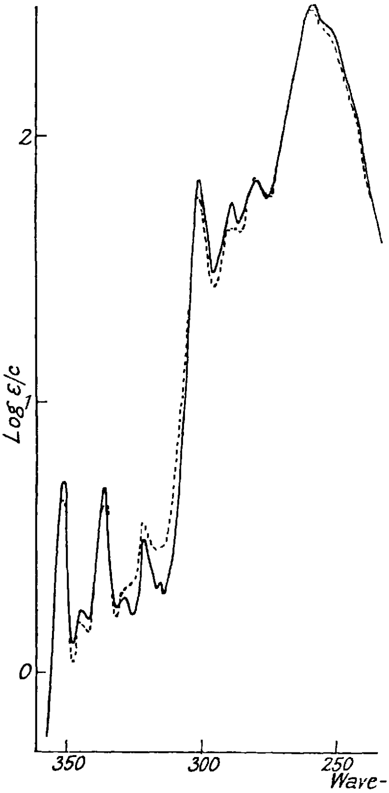
Dr. R. K. Callow and Mr. F. A. Askew, of the National Institute for Medical Research, have kindly measured the ultra-violet absorption spectra of the new hydrocarbon, of the two pure samples of Diels's hydrocarbon (one prepared from cholesterol, the other from ergosterol), and of *cyclo*pentenophenanthrene, by the method of Philpot and Schuster (Medical Research Council Special Report Series, No. 177, 1933). These are shown in Figs. 1 and 2 in terms of log ε/c, where $\varepsilon = 1/d \,.\, \log_{10} I_0/I - \varepsilon_0$ and c is the concentration in grams per litre. The agreement between the curves in Fig. 1 is good; there are, however, minor differences of approximately the same order as those existing between the two samples of Diels's hydrocarbon.

Finally, crystallographic measurements have been carried out by Mr. J. D. Bernal, who finds that the synthetic material agrees with Diels's preparation within the limits of experimental error; his results are embodied in a note which will be published shortly.

Thus there appears to be little doubt that Diels's hydrocarbon is identical with our synthetic material; and that its structure is correctly represented by the formula (II), unless some unforeseen and profound change takes place in the final dehydrogenation of the hydrocarbon (IX). It is proposed to confirm this conclusion by the preparation of the nitro-compound $C_{18}H_{13}O_2N$ (Diels, Gädke, and Körding, *Annalen*, 1927, **459**, 1) as soon as a sufficient quantity of the synthetic hydrocarbon has been accumulated.

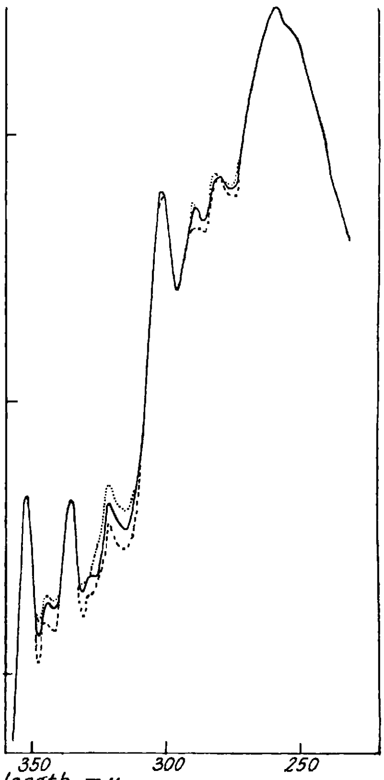
The substance prepared by Bergmann and Hillemann's method, on the other hand, shows several points of distinction from our synthetic material; it crystallises in needles, not plates, and the higher melting point of the picrate cannot be neglected even though the picrates of this series of compounds are unstable and difficult to obtain pure for this reason. The trinitrotoluene derivative also melts a few degrees high. At the same time, Mr. Bernal's measurements show no essential difference between the two preparations; we therefore prefer to reserve judgment until a larger quantity of Bergmann and Hillemann's compound has been prepared.

FIG. 1.



—— *cyclo*Pentenophenanthrene.
\- - - - 3-Methyl*cyclo*pentenophenanthrene.

FIG. 2.



····· $C_{18}H_{16}$ from ergosterol.
—— $C_{18}H_{16}$ from cholesterol.
\- - - - 3-Methyl*cyclo*pentenophenanthrene.

The mechanism by which the compound $C_{18}H_{16}$ is formed from cholane derivatives is still obscure and a discussion of it is reserved until further experiments bearing on the matter have been completed.

EXPERIMENTAL.

2-*Methyl*-1-β-(α-*naphthyl*)*ethyl*cyclo*pentanol* (III).—To an ice-cold Grignard solution prepared from 90 g. of β-(α-naphthyl)ethyl bromide and 9 g. of magnesium (activated by iodine), 43 g. of 2-methyl*cyclo*pentanone were added drop by drop with mechanical stirring, the mixture was finally warmed for ½ hour, and ice and acetic acid added. The ethereal extract, dried over potassium carbonate, gave 24·4 g. of the desired *alcohol*, b. p. about 190°/3 mm., as a colourless, very viscous liquid (Found: C, 84·9; H, 8·5. $C_{18}H_{22}O$ requires C, 85·0; H, 8·7%). There was also a fraction, b. p. about 240°/3 mm., which solidified and had m. p. 102° after several crystallisations from benzene; it was evidently αδ-*di-(α-naphthyl)butane* (Found: C, 92·6; H, 7·3. $C_{24}H_{22}$ requires C, 92·8; H, 7·2%); the dipicrate had m. p. 174°, the bis-*s*-trinitrobenzene compound m. p. 187°, and the *bistrinitrotoluene* compound m. p. 131° (Found: C, 59·6; H, 4·4. $C_{38}H_{32}O_{12}N_6$ requires C, 59·5; H, 4·2%).

1-*Methyl*-1 : 2-cyclo*pentano*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (VI).—24 G. of the alcohol (III) were heated for 40 minutes with 40 g. of phosphoric oxide at about 140° under reduced pressure. The cooled mixture was treated with ice, and the *hydrocarbon* isolated by means of ether and distilled, finally over sodium; b. p. 155°/0·4 mm., $d_4^{18.9^\circ}$ 1·04552, n_D 1·61363, $[R_L]_D$ 78·68. It was a colourless viscous liquid with a fine blue fluorescence; it still contained some unsaturated material, as it decolorised bromine in chloroform solution to some extent; this no doubt accounts for the somewhat high molecular refraction observed (Found: C, 91·2; H, 8·5. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%).

Dehydrogenation. This was carried out as described in Part I (*loc. cit.*); the product was readily isolated and after distillation proved to be almost pure *cyclo*pentenophenanthrene; the pure compound was obtained from it by repeated crystallisation from alcohol (charcoal) (Found: C, 93·3, 93·5; H, 6·4, 6·7. Calc.: C, 93·6; H, 6·4%). The picrate (Found: C, 61·8, 61·9; H, 3·9, 3·9. Calc.: C, 61·7; H, 3·8%) and the trinitrobenzene compound (Found: C, 64·3, 64·4; H, 4·1, 4·1. Calc.: C, 64·0; H, 4·0%) were also prepared and compared with genuine specimens.

1-*Methyl*-2-β-(α-*naphthyl)ethyl*cyclo*pentanol* (VII).—2-β-(α-Naphthyl)ethyl*cyclo*pentanone (16·5 g.) was treated with an excess of methylmagnesium iodide in ether, and the product isolated as above. It was shaken with semicarbazide acetate solution to remove unchanged ketone and, being indistillable owing to excessive frothing, was used for the preparation of the hydrocarbon. This was purified as before and had b. p. 154°/0·3 mm., $d_4^{17.6^\circ}$ 1·06338, n_D 1·61991, $[R_L]_D$ 78·00; it was fully saturated (Found: C, 90·9; H, 8·5%).

Dehydrogenation. This proceeded exactly as before and gave a good yield of *cyclo*pentenophenanthrene, which was identified as before; the *trinitrotoluene* compound formed fine yellow needles, m. p. 102° (Found: C, 64·7; H, 4·4. $C_{24}H_{19}O_6N_3$ requires C, 64·7; H, 4·3%) (compare L. Ruzicka, Goldberg, Ehmann, and Hösli, *loc. cit.*).

2 : 5-*Dimethyl*cyclo*pentanone.*—The ketone was prepared by the method of Haller and Cornubert (*Compt. rend.*, 1924, **179**, 315); we find that the semicarbazone melts at 190—191°.

2 : 5-*Dimethyl*-1-β-(α-*naphthyl)ethyl*cyclo*pentanol* (VIII).—This was prepared from the above ketone (40 g.) exactly as in the case of the lower homologue, 31 g. of the *alcohol* being collected at 190—195°/0·2 mm. (Found: C, 85·0; H, 9·3. $C_{19}H_{24}O$ requires C, 85·1; H, 9·0%).

1 : 3′-*Dimethyl*-1 : 2-cyclo*pentano*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (IX).—The dehydration of the alcohol was carried out as described above, giving a good yield of the *hydrocarbon*, a colourless viscous liquid with a blue fluorescence. On redistillation over sodium, a small low fraction containing unsaturated material was collected separately; the main body had b. p. 160°/0·4 mm., $d_4^{18.2^\circ}$ 1·04203, n_D 1·60681, $[R_L]_D$ 82·89, and was saturated (Found: C, 91·4; H, 9·0. $C_{19}H_{22}$ requires C, 91·1; H, 8·9%).

Dehydrogenation. 18·5 G. of the above hydrocarbon were heated with selenium as before; the product gave on distillation 10 g. of a solid hydrocarbon mixture. This was recrystallised from alcohol (charcoal) and converted into the *trinitrobenzene* derivative, which was recrystallised from alcohol until the melting point was constant (145—146°) (Found: C, 64·7; H, 4·5. $C_{24}H_{19}O_6N_3$ requires C, 64·7; H, 4·3%). The *hydrocarbon* (II) was regenerated from a boiling alcoholic solution of this by addition of an excess of stannous chloride in hydrochloric acid, boiling for a short time, addition of water, and extraction with ether (Cook and Hewett, *loc. cit.*). After repeated crystallisation from alcohol it melted at 125—126° (Found: C, 93·1; H, 6·8. $C_{18}H_{16}$ requires C, 93·1; H, 6·9%). The *picrate* formed flattened brownish-orange needles with a coppery reflex, m. p. 118—119° (Found: C, 63·1; H, 4·1. $C_{24}H_{19}O_7N_3$ requires C, 62·5; H, 4·1%); the compound is readily split into its components on repeated crystallisation. The *trinitrotoluene* compound formed characteristic, pale yellow, flattened needles with a greenish tinge, m. p. 93° (Found: C, 65·2; H, 4·6. $C_{25}H_{21}O_6N_3$ requires C, 64·7; H, 4·3%).

A second *hydrocarbon* was present in the original dehydrogenation product in small amount, but we have not yet obtained it pure; it is characterised by its relatively sparing solubility in light petroleum and melts at 230° (Found: C, 93·3; H, 6·1. $C_{18}H_{14}$ requires C, 93·9; H, 6·1%). It forms a scarlet picrate, needles, m. p. 134—135°; the amount available did not permit final purification (Found: C, 50·4; H, 3·0%).

Hydrocarbon $C_{18}H_{16}$ *prepared by Bergmann and Hillemann.*—The preparation was carried out exactly as described (*loc. cit.*); great difficulty was experienced in the reduction of the unsaturated ester. The hydrocarbon differed in properties from that described above; thus, it would not crystallise from alcohol at first, and acetic acid, the solvent recommended by Bergmann and Hillemann, had to be employed. Solutions of this hydrocarbon in all solvents became cloudy before crystallisation began; when pure, the compound formed small needles, m. p. 125° (Found: C, 92·8; H, 6·9. Calc.: C, 93·1; H, 7·0%). The trinitrobenzene compound had m. p. 147—148°, and the trinitrotoluene compound, 96—97°.

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