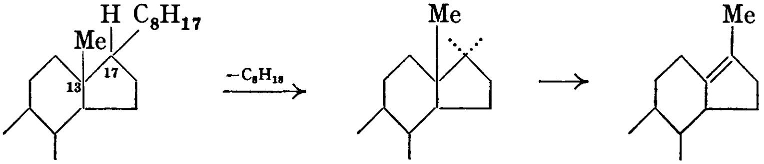
219. *Further Experiments on the Thermolysis of Cholesteryl Chloride.*

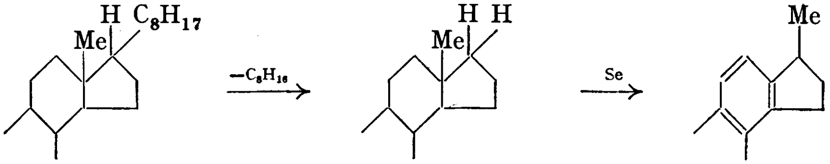
By Ernst Bergmann and Felix Bergmann.

The migration of the C_{13} methyl group in the dehydrogenative conversion of steroids into 3′-methyl*cyclo*pentenophenanthrene takes place during the thermal decomposition of the steroid molecule and is not necessarily connected with the dehydrogenation. This conclusion is drawn from the results of experiments on the structure of the two products, $C_{19}H_{30}$ and $C_{15}H_{22}$, obtained by thermolysis of cholesteryl chloride.

In a preliminary note (*Chem. and Ind.*, 1936, **55**, 272) it was pointed out that the formation of 3′-methyl-1 : 2-*cyclo*pentenophenanthrene on dehydrogenation of steroids appears to be a two-stage process : (*a*) thermolytic formation of octane and of a bivalent radical at C_{17}, followed by retropinacolic stabilisation, which involves migration of the C_{13}-methyl group, and (*b*) dehydrogenation :



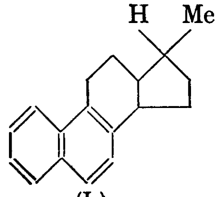
An alternative possibility is given by the following scheme :



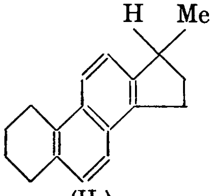
Here, the steroid molecule is split into one molecule of octene and a residue saturated at C_{17} ; in this case, migration of the C_{13}-methyl group would occur in the course of dehydrogenation only. This possibility has to be borne in mind in view of the results of Linstead and co-workers (J., 1937, 1146), who observed, under certain conditions, the formation of α-methylnaphthalene from 9-methyl-Δ^1-octalin (which, however, contains a double bond).

The experiments reported seem to show that the former alternative is correct, since the C_8-compound split off during thermolysis is mainly octane although some unsaturated material also is present. The proof, therefore, must be sought in the nature of the two hydrocarbons $C_{19}H_{30}$ and $C_{15}H_{22}$, previously described (*loc. cit.*), which we have now investigated in greater detail.

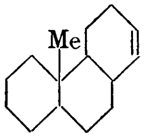
The substance $C_{19}H_{30}$ is a tetracyclic hydrocarbon containing one double bond. Oxidative fission at this vulnerable point could not be effected, but catalytic hydrogenation eventually gave a *hydrocarbon* $C_{19}H_{32}$: obviously the double bond is in a masked position. Dehydrogenation gave, *inter alia*, 3′-methyl*cyclo*pentenophenanthrene and a *hydrocarbon* $C_{18}H_{20}$. The production of the former is not a proof of the presence of the 3′-methyl group in the hydrocarbon $C_{19}H_{30}$, for Linstead's observation invalidates the evidence : in view of the results obtained with $C_{15}H_{22}$ (see below), however, the conclusion seems justified. The hydrocarbon $C_{18}H_{20}$, therefore, which gives a dark red coloration with picric acid solution, indicating the presence of a naphthalene system, must have formula (I) or (II).



(I.)



(II.)



+ 1 other double bond

(III.)

Dehydrogenation of the hydrocarbon $C_{15}H_{22}$ gave phenanthrene and a liquid hydrocarbon, $C_{14}H_{18}$ or $C_{15}H_{20}$. The production of phenanthrene under these conditions shows that a methyl group is not present at C_2 of the phenanthrene system (C_{13} of the sterol skeleton) in $C_{15}H_{22}$—otherwise 2-methylphenanthrene would have been formed—and is further a proof for the formula $C_{15}H_{22}$ and against $C_{16}H_{24}$, which could not be excluded on the basis of the experiments reported in our preliminary paper : if the latter formula were correct, two methyl groups would have had to have been eliminated in the phenanthrene formation, which is unlikely. The hydrocarbon $C_{15}H_{22}$, therefore, is to be formulated as (III).

The physical constants of the liquid hydrocarbon $C_{14}H_{18}$ or $C_{15}H_{20}$ are in satisfactory agreement with those reported for 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene ($C_{14}H_{18}$) by Schroeter (*Ber.*, 1924, **57**, 1990, 2025; compare Auwers and Krollpfeiffer, *Annalen*, 1922, **430**, 253); in its formation from $C_{15}H_{22}$ the double bond migrates from ring C into ring B, which becomes aromatic. The formula $C_{15}H_{20}$ is not definitely excluded; as it would include the quaternary methyl group present at C_{10} of the sterol skeleton, only ring C could become aromatic.

How could a hydrocarbon $C_{15}H_{22}$ (III) be formed subsequently to $C_{19}H_{30}$? Apparently, the five-membered ring of the original sterol skeleton is split off as a whole, probably after one-sided fission of the hydrindene system such as occurs in the formation of chrysene from steroids and of 7-methylnaphthafluorene from strophanthidin (E. Bergmann, *J. Amer. Chem. Soc.*, 1938, **60**, 2306). If so, the absence of the C_{13} methyl group from the fission product $C_{15}H_{22}$ is only understandable if it had already changed its position in the starting material $C_{19}H_{30}$; otherwise, it should have survived the fission. The reaction mechanism proposed therefore seems plausible.

By the thermolysis of cholesterol Fischer and Treibs (*Annalen*, 1925, **446**, 1241) obtained *inter alia*, a substance $C_{15}H_{12}$, m. p. 91—92°, which gave a dark yellow picrate, m. p. 155°. This substance is probably 9-methylphenanthrene. It may have been formed from the thermolysis product $C_{15}H_{22}$ by spontaneous aromatisation, but the methyl group is not eliminated as in the case of selenium dehydrogenation; it migrates in a manner analogous to the oxidative conversion of ergosterol into toluenetetracarboxylic acid (Inhoffen, Guiferas, and Nakameya, *Annalen*, 1932, **494**, 122; Reindel and Niederländer, *ibid.*, 1930, **482**, 264; compare also Haworth, J., 1934, 454; Jones and Ramage, J., 1938, 1853).

A second substance, $C_{18}H_{14}$, m. p. 203°, described by Fischer and Treibs, seems to be impure chrysene, which is a common degradation product of sterols (Diels and co-workers, *Annalen*, 1927, **459**, 1; 1930, **478**, 129; *Ber.*, 1927, **60**, 140; 1933, **66**, 487; Ruzicka and co-workers, *Helv. Chim. Acta*, 1934, **17**, 200; Raudnitz *et al.*, *Z. physiol. Chem.*, 1932, **209**, 103; *Ber.*, 1933, **66**, 879; Butenandt and Thompson, *Ber.*, 1934, **67**, 140). We have often observed that chrysene so formed has a rather low m. p., which can be raised only with difficulty.

EXPERIMENTAL.

Experiments with $C_{19}H_{30}$.—When a benzene solution (5%) was passed through a column of calcium hydroxide (35 cm. in height), it lost its fluorescence but retained practically the whole of the hydrocarbon. The refractive index changed from 1·5263 to 1·5250.

Hydrogenation. The hydrocarbon (4·8 g.) in butanol (100 c.c.) was hydrogenated in presence of palladised barium sulphate, which had to be re-activated several times by passage of air through the apparatus. The main *product*, b. p. 169—174°/1 mm., $n_D^{18°}$ 1·5210, gave analytical figures consistent with the formula $C_{19}H_{32}$, indicating the presence of one double bond in the original material (Found : C, 87·6, 87·5; H, 12·1, 12·2. $C_{19}H_{32}$ requires C, 87·7; H, 12·3%). The residue left after distillation partly crystallised. The crystals were recrystallised from glacial acetic acid or xylene and formed needles, m. p. 246·5°, the analysis of which pointed to the formula $C_{19}H_{20}O_4$, the presence of the oxygen being apparently due to catalytic oxidation (Found : C, 73·0; H, 6·1. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·4%).

Dehydrogenation. The hydrocarbon was heated with twice its weight of selenium in sealed tubes at 300—320°. The experiments were made with small batches, in order to avoid too high a pressure in the tubes, and the products combined. The following fractions were obtained: (a) B. p. 115°/0·18 mm. This substance was 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene according to its refractive index, $n_D^{18°}$ 1·5631 (Found : C, 90·1; H, 9·7; *M*, 166.

Calc. for $C_{14}H_{18}$: C, 90·3; H, 9·7%; *M*, 186). It was also formed on dehydrogenation of the hydrocarbon $C_{15}H_{22}$.

(b) B. p. 130°/0·6 mm. This fraction was a colourless fluorescent oil which darkened on standing; $n_D^{20 \cdot 3°}$ 1·5962. Its analysis (Found: C, 90·9; H, 8·8; *M*, 215. Calc. for $C_{14}H_{16}$: C, 91·3; H, 8·7%; *M*, 184. Calc. for $C_{15}H_{18}$: C, 90·9; H, 9·1%; *M*, 198) indicated a hexahydrophenanthrene or a methyl derivative.

(c) B. p. 150—180°/0·2 mm. This product solidified almost completely, forming colourless crystals exhibiting a violet fluorescence. It separated from alcohol in needles, m. p. 124—125°, which were identified as 3′-methyl-1 : 2-*cyclo*pentenophenanthrene by means of the trinitrobenzene compound, m. p. 149° (Gamble, Kon, and Saunders, J., 1935, 644) (Found: C, 64·6; H, 4·1; N, 9·7. Calc.: C, 64·7; H, 4·3; N, 9·4%).

(d) B. p. 180—190°/0·18 mm. This was a greenish-yellow liquid (Found: C, 91·2; H, 8·8; *M*, 262. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%; *M*, 236). A C_{19} formula would account for the presence of an aromatic naphthalene system (coloration with picric acid) only if the C_{10} methyl group had migrated, *e.g.*, to the para-position, as in the conversion of ergosterol into toluenetetracarboxylic acid (see above), which is not very likely.

Experiments with $C_{15}H_{22}$.—The hydrocarbon (1 g.) was heated with selenium (2 g.) for 36 hours at 275—300° (sealed tube). Three fractions were obtained in a high vacuum (0·2 to 0·5 mm.): (a) B. p. 120—125°. Unchanged material (Found: C, 88·6; H, 10·6. Calc.: C, 89·1; H, 10·9%).

(b) B. p. 125—135°. Analysis pointed to the formula $C_{14}H_{18}$ (Found: C, 90·2; H, 10·0. Calc.: C, 90·3; H, 9·7%) of the afore-mentioned octahydrophenanthrene.

(c) B. p. 165° (bath temperature). This fraction formed white crystals, m. p. 90°, not depressed by phenanthrene, but markedly depressed by 9-methylphenanthrene.

9-Methylphenanthrene was prepared by heating phenanthryl-9-aldehyde semicarbazone (Shoppee, J., 1933, 40) (2 g.) with sodium ethoxide solution (2 g. of sodium, 40 c.c. of alcohol) at 200° for 6 hours (autoclave; nitrogen atmosphere). Dilute sulphuric acid and ether were added, and the hydrocarbon isolated in the usual way. After crystallisation from propyl alcohol, it had m. p. 99·5°.

9-Methylphenanthrene depresses the m. p. of phenanthrene to 64—68°, but their picrates (m. p. 153° and 145° respectively) give no m. p. depression with each other (compare Haworth, *Ann. Reports*, 1937, 329; Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1938, **60**, 1658).

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[*Received, March 9th*, 1939.]