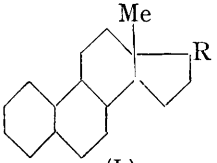
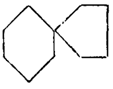
164. *The Action of Selenium on Compounds containing Angular Methyl Groups.*

By George R. Clemo and Haydn G. Dickenson.

The wide use of selenium dehydrogenation (Diels, *Ber.*, 1927, **60**, 2323) in elucidating the skeletal structures of many naturally occurring organic compounds, especially terpenes and sterols, renders it important to investigate the limitations of the method. It is drastic, and a typical case of a misleading result due to a structural change is the production of chrysene from cholesterol, which is now known to embody a *cyclo*pentenophenanthrene skeleton (I) and not that of chrysene. The latter is presumably produced by a ring enlargement involving the angular methyl group.



(I.)



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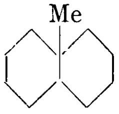

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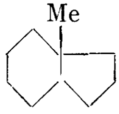
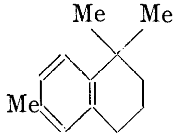


(IV.)

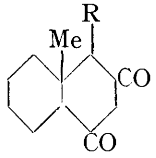
In the dehydrogenation of the sterols there is also produced a hydrocarbon, $C_{18}H_{16}$, known as Diels's hydrocarbon. This has now been identified with 3'-methyl-1 : 2-*cyclo*pentenophenanthrene, which presumably arises from the loss of R, and the wandering of the methyl group from the angular to the 3'-position in the *cyclo*pentenophenanthrene skeleton.

Clemo and Ormston (J., 1933, 352) showed that ring structural changes did occur, as they obtained naphthalene by the dehydrogenation of *cyclo*hexane*spirocyclo*pentane (II) with selenium at 280—330°, and it was proposed to continue this work by studying the selenium dehydrogenation of compounds containing angular methyl groups, in particular, 9-methyldecalin (III) (Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, 1931, **14**, 1154) and 8-methylhydrindane (IV). 1 : 1 : 6-Trimethyltetralin (V) also has been investigated.



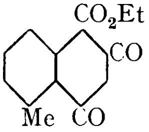
(V.)

(VI.)

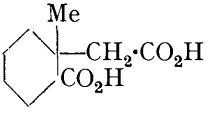


(VII.)

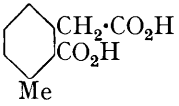
Ruzicka's synthesis of (III) was as follows: 2-acetyl-1-methyl-Δ^1-*cyclo*hexene (VI) was condensed with sodiomalonic ester to give the diketo-ester (VII) (R = CO_2Et), which, on hydrolysis, gave the diketone (VII, R = H). This, on reduction by Clemmensen's method, gave 9-methyl-*trans*-decalin (III). No proof of the structure of the diketone (VII, R = H) was advanced save that it was oxidised to a dibasic acid, the methyl ester of which gave the analytical results required for that of (IX). There is therefore a possibility that the double bond in (VI) might have migrated before the Michael addition to give (VIII) instead of (VII, R = CO_2Et), which would ultimately yield 1-methyl-*trans*-decalin.



(VIII.)



(IX.)



(X.)

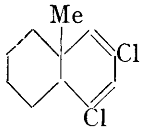
The synthesis has been repeated and the compounds (VII, R = H and CO_2Et), hitherto isolated as impure oils, have been obtained crystalline, m. p. 127—129° and 129—130° respectively. They give correct analytical results if special precautions are taken, but are apt to give a low value for carbon, possibly due to a tendency for the angular methyl group to escape as methane.

The diketone, whether derived from (VII) or (VIII), is a strong acid and is remarkable in giving no evidence for the presence of reactive keto- or methylene groups when treated with piperonal, semicarbazide, or *o*-aminobenzaldehyde. It is readily oxidised by hypobromite to the *cis*-form of the dicarboxylic acid (IX) or (X), but permanganate gives only a very poor yield of a different acid. In an attempt to decide between formulæ (IX) and (X) by heating the *cis*-acid with selenium, whereby toluene and *m*-xylene respectively might be expected to result, the acid was recovered as the stable anhydride.

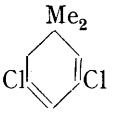
The hydrocarbon was then obtained as described by Ruzicka and had a characteristic odour, quite distinct from that of 1-methyldecalin. All attempts to dehydrogenate it failed, it being recovered unchanged after being heated for 100 hours with selenium at 280—330°. A very small amount of material boiled slightly higher and gave the analytical results required for $C_{10}H_{16}$. It was thought to be 9 : 10-octalin, but the characteristic dibromide could not be obtained. Dehydrogenation was then attempted by the method of Ehrenstein (*Ber.*, 1931, **64**, 1137) with a platinum catalyst and, though decalin and 1-methyldecalin were converted readily into naphthalene and 1-methylnaphthalene respectively in this way, the hydrocarbon in question was unattacked. Sulphur (which led to much decomposition), sulphur and selenium, and selenium dioxide were also ineffective.

When the diketone was treated with phosphorus pentachloride in chloroform, it gave a *dichloro*-compound (XI) which, when heated with selenium, gave 1-methylnaphthalene. The conclusion drawn from this rather surprising result is that the diketone is (VII, R = H) and gives 9-methyl-*trans*-decalin as claimed by Ruzicka.

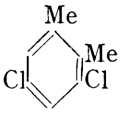
Whether the methyl group migrates into the unsaturated ring during the preparation of the dichloro-compound or in the subsequent heating is not known, as the various migrations furnish inconclusive evidence on the point. These migrations are similar to the conversion of 3 : 5-dichloro-1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene (XII) (Crossley and Le Sueur, J., 1902, **81**, 1536) into 3 : 5-dichloro-*o*-xylene (XIII).



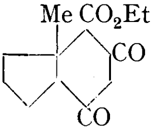
(XI.)



(XII.)



(XIII.)



(XIV.)

2-Acetyl-1-methyl-Δ^1-*cyclo*pentene condenses readily with sodiomalonic ester to give the diketohydrindane derivative (XIV), which, on hydrolysis and reduction, gives 8-*methyl*-trans-*hydrindane* (IV). The yields are better than in the case of 9-methyldecalin. The hydrocarbon has a terpene-like odour and, as in the previous case, all attempts to dehydrogenate it failed, the original substance being recovered in each case and no evidence found for its conversion into either naphthalene or methylindene.

The diketone obtained from (XIV) gave a dichloro-compound as in the previous case, but this, on treatment with selenium, gave no recognisable products, only a minute amount of a non-picrate-forming oil being isolated.

The hydrocarbon (V) obtained by ring closure of α-ionone (Tiemann and Kruger, *Ber.*, 1893, **26**, 2683) was heated with selenium at 290—310° and gave a good yield of 1 : 6-dimethylnaphthalene (compare also Ruzicka and Rudolph, *Helv. Chim. Acta*, 1927, **10**, 916), there being no evidence of a migration from the 1-position.

EXPERIMENTAL.

9-*Methyldecalin.*—The diketo-ester (VII, R = CO_2Et) was prepared as described by Ruzicka (*loc. cit.*) except that the ethereal extract of the reaction mixture was extracted twice with sodium carbonate solution. The combined carbonate extracts on acidification yielded the diketo-ester as a pale yellow oil, which solidified after 1—2 hours (yield, 50%). It was recrystallised from dilute alcohol, giving small colourless prisms, m. p. 127—129° [Found : C, 66·2; H, 8·2; *M* (Rast), 256. Calc. for $C_{14}H_{20}O_4$: C, 66·7; H, 7·9%; *M*, 252].

The above ester (30 g.) was hydrolysed by boiling with 20% alcoholic potash (150 c.c.) on the water-bath for 8 hours. The product was diluted with water, the alcohol removed, the residue acidified (hydrochloric acid), and the 2 : 4-diketo-9-methyldecalin extracted with ether. On distillation it was obtained as a faintly yellow, glassy resin (17 g.), b. p. 155°/0·3 mm. This solidified with difficulty and then crystallised from petroleum–benzene in minute colourless prisms, m. p. 129—130° (Found : C, 72·7; H, 8·9. Calc. for $C_{11}H_{16}O_2$: C, 73·3; H, 8·9%). A molecular-weight determination by the method of Rast indicated considerable association.

9-Methyldecalin was obtained by reducing the above diketone as described by Ruzicka (*loc. cit.*).

Attempted Dehydrogenation of 9-*Methyldecalin.*—The hydrocarbon (0·9 g.) was heated with selenium (4 g.) at 260—280° for 12 hours and at 300—340° for a further 36 hours. The residue consisted of the original hydrocarbon (0·6 g.) and a higher-boiling fraction (0·1 g.), b. p. 82—84°/18 mm. This was treated with picric acid (0·15 g.) in alcohol (1 c.c.), but only picric acid (0·075 g.) crystallised, even after concentration of the solution. The recovered hydrocarbon was again treated with selenium for a further 48 hours, but only a small amount of the liquid, b. p. 82—84°/18 mm., was isolated (Found : C, 88·1; H, 11·9. $C_{10}H_{16}$ requires C, 88·2; H, 11·8%).

Dichloro-compound (XI).—The diketone (above) was treated with 1½ times the theoretical quantity of phosphorus pentachloride in chloroform. After 2—3 hours' refluxing, the excess of the pentachloride was decomposed with water, the chloroform removed, and the product fractionated. The *dichloro*-compound boiled at 150—155°/13 mm. (Found : C, 60·4; H, 6·2. $C_{11}H_{14}Cl_2$ requires C, 60·8; H, 6·45%).

Dehydrogenation of the Dichloro-compound.—The compound (2 g.) with selenium (4 g.) was heated at 280—300° for 60 hours. The residue was extracted with chloroform, the solution filtered (charcoal), the solvent removed, and the oil dissolved in light petroleum and again filtered from selenium. On distillation over sodium it yielded a hydrocarbon (0·8 g.), b. p. approx. 110°/12 mm., which gave a bright yellow picrate, m. p. 140—141°, not depressed by admixture with 1-methylnaphthalene picrate (Found : C, 54·7; H, 3·75. Calc. for $C_{17}H_{13}O_7N_3$: C, 55·0; H, 3·5%).

2-*Carboxy*-1-*methyl*cyclo*hexane*-1-*acetic Acid* (IX).—The *cis*-acid was obtained by oxidation of the diketone with hypobromite (Ruzicka, *loc. cit.*). It crystallised well from water in small prisms, m. p. 172—173° (Found : C, 60·2; H, 8·25. Calc. for $C_{10}H_{16}O_4$: C, 60·0; H, 8·0%).

Attempted Dehydrogenation of the cis-*Acid.*—The acid (1·6 g.) was heated with selenium in a flask with a sealed-on water-cooled condenser at 280—300° for 24 hours and at 330° for a further 36 hours. The residue consisted of unchanged acid (as the anhydride) and a trace of a liquid, b. p. approx. 110°/760 mm. When the ester was used in place of the acid, it was recovered unchanged.

8-*Methylhydrindane* (IV).—2-Acetyl-1-methyl-Δ^1-*cyclo*pentene was obtained, in rather poor yield, either by the method of Perkin and Marshall (J., 1890, **57**, 242) or by the method used above starting from methyl-Δ^1-*cyclo*pentene. The latter method is superior if the ketone is to be made in quantity; it is then obtained as an oil, b. p. 191°/760 mm.

Ethyl 2 : 4-diketo-8-methylhydrindane-1-carboxylate was obtained in a similar manner to the decalin compound (above.) The yield is better (50—60%), but the diketo-ester has been obtained only as a yellowish glassy resin, b. p. 150—160°/0·3 mm. It was hydrolysed by refluxing with alcoholic potash as above, and after distillation 2 : 4-*diketo*-8-*methylhydrindane* (b. p. 143°/0·3 mm.) gradually solidified; it crystallised from petroleum–ether in colourless prisms, m. p. 91—92° (Found : C, 72·9; H, 8·7. $C_{10}H_{14}O_2$ requires C, 72·4; H, 8·45%). The diketone (4 g.) was refluxed with amalgamated zinc (40 g.) and concentrated hydrochloric acid (40 c.c.) for 14 hours, fresh acid being added at intervals. The product was extracted with ether, washed with alkali and water, and fractionated over potassium, pure 8-*methylhydrindane* being obtained as a colourless liquid (1 g.), b. p. 159—160°/760 mm. (Found : C, 87·5; H, 12·7. $C_{10}H_{18}$ requires C, 87·0; H, 13·0%).

Dichloro-compound from 2 : 4-*Diketo*-8-*methylhydrindane*.—This diketone yielded, in exactly the same way as the previous diketone (VII, R = H), a *dichloro*-compound, which was isolated as an oil, b. p. 109—110°/12 mm. (Found: C, 59·0; H, 6·3. $C_{10}H_{12}Cl_2$ requires C, 59·1; H, 5·9%).

Attempted Dehydrogenation of the Above Dichloro-compound.—The substance (1 g.) was heated with selenium (2 g.) at 280—300° for 24 hours. There was much decomposition, and extraction of the product yielded a very small amount of oil which did not give a picrate or condense with piperonal as would be expected had it been an indene derivative.

1 : 1 : 6-*Trimethyltetralin*.—This compound was obtained as an oil, b. p. 130°/30 mm., as described in the literature. It was dehydrogenated with selenium in the usual way and gave a 60% yield of 1 : 6-dimethylnaphthalene (picrate, orange needles, m. p. and mixed m. p. 110—111°).

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