113. *Fused Carbon Rings. Part VIII. The Dehydration of 2-Methyl-*1*-$\Delta^{3'}$-butenyl*cyclo*hexanol.*

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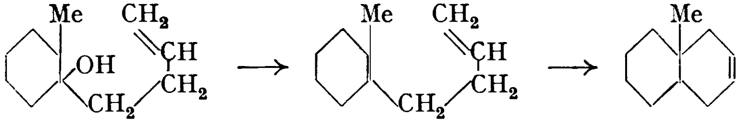
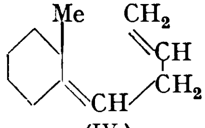
A STUDY of the dehydration of *2-methyl-*1*-$\Delta^{3'}$-butenyl*cyclo*hexanol* (I), isomeric with 1-methyl-2-$\Delta^{3'}$-butenyl*cyclo*hexanol [(XI) in the preceding paper], has given results of some theoretical interest. The alcohol (I) is readily obtained by the interaction of butenyl-magnesium bromide with 2-methyl*cyclo*hexanone. When heated with phosphoric acid at 130° under the conditions which rapidly cyclise its isomeride, it yields a mixture of hydrocarbons consisting mainly of the monocyclic diene, 2-*methyl*-1-Δ$^{3'}$-*butenyl*cyclo*hexene* (II). By prolonging the time of heating, more cyclisation occurs with the formation of *cis*-9-methyl-Δ^{2}-octalin (III). This octalin is formed to the exclusion of the diene when the alcohol (I) is heated at 150° with a mixture of phosphoric acid and its anhydride.


(I.) (II.) (III.)


(IV.)

The product resembled in its physical properties the *cis*-9-methyloctalin described in Part VII (preceding paper) and on oxidation yielded the same two 1-methyl*cyclo*hexane-1 : 2-diacetic acids. Both these acids (m. p.'s 163° and 192°) yielded neutral esters on rapid esterification with methyl-alcoholic sulphuric acid and it is therefore improbable that either of them contains a tertiary carboxyl group (contrast 1-methyl-Δ^{2}-*cyclo*hexene-1 : 2-dicarboxylic acid, p. 483). This supports the Δ^{2}-structure for the octalin. The 8-methyl-2-hydrindanone obtained on cyclisation was practically pure *cis*-compound; it gave a semicarbazone, m. p. 219°, and on oxidation with nitric acid *cis*-1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid, identical with that of Part VII. The isomeric *trans*-acid could not be detected. These results agree with the *cis*-9-methyloctalin structure for the original hydrocarbon, but it is necessary to make the same reservations as to the possible presence of 8-methyloctalin as in the preceding paper.

The results described here and in Part VII present some interesting contrasts with those obtained by Bogert, Davidson, and their collaborators in their important study of the *cyclo*-dehydration of alcohols containing a carbon chain of 5—7 carbon atoms terminated by a phenyl group (*J. Amer. Chem. Soc.*, 1934, **56**, 185, 959; 1935, **57**, 151). These substances yield tetralins and/or indanes on treatment with sulphuric or phosphoric acid. Although a strict comparison is not yet possible, it appears that there is a greater latitude in the type of structure capable of cyclising when an aromatic ring is involved. The formation of a *cyclo*pentane ring in the case of the indanes has as yet no parallel among purely hydroaromatic compounds.

There appears to be no doubt that the formation of 9-methyloctalin from 2-methyl-1-butenyl*cyclo*hexanol passes through the stage of the diene (II). The cyclisation of this diene by phosphoric acid at 130° is slow compared with that of 1-methyl-2-butenyl*cyclo*hexanol. Hence it is very probable that the formation of octalin from the latter involves a direct *cyclo*-dehydration. The facts could, however, be explained if 1-methyl-2-butenyl*cyclo*hexanol were dehydrated to (II), which cyclised readily, whereas its isomeride (I) yielded the diene (IV), which could only yield an octalin after isomeric change, *e.g.*, to (II). The rate-determining process would then be the change (IV) ⟶ (II). This explanation, although unlikely, is not excluded by the experimental evidence. It is of interest that in the aromatic series Bogert and Davidson (*loc. cit.*) conclude that both cyclisation through the diene stage and direct *cyclo*-dehydration can occur, but that the former is the usual mechanism.

The most promising result from the dehydration of cyclic butenyl compounds is that it leads to the formation of decalins of the same configuration (*cis*-) as that present in many dicyclic sesquiterpenes (Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, 1931, **14**, 1171). The application of the new method to the synthesis of substances related to these and to the sex-hormones is in hand; also the cyclisation of analogous substances without a potential angular methyl group.

EXPERIMENTAL.

An ethereal solution of 56 g. (0·5 mol.) of 2-methyl*cyclo*hexanone was added to the well-stirred Grignard reagent prepared from 67 g. (0·5 mol.) of Δ^{3}-butenyl bromide and 12 g. of magnesium in 400 c.c. of dry ether. The mixture was refluxed over-night and poured on ice and acetic acid, and the aqueous solution extracted with ether. The ethereal solution was washed with sodium carbonate, dried, and evaporated. After the recovery of some unchanged ketone, 2-*methyl*-1-$\Delta^{3'}$-*butenyl*cyclo*hexanol* (I) distilled at 98—108°/18 mm.; after redistillation it had b. p. 104—108°/18 mm., $n_D^{16\cdot5^\circ}$ 1·4784, $d_{4^\circ}^{16\cdot5^\circ}$ 0·9239, $[R_L]_D$ 51·56 (calc., 51·86) (Found: C, 78·0; H, 11·5. $C_{11}H_{20}O$ requires C, 78·5; H, 11·9%).

Dehydration. When 5 g. of the alcohol were shaken with 24 c.c. of syrupy phosphoric acid, the temperature rose to about 40°. The mixture was heated at 130° (oil-bath) for 1 hour, and the product isolated as described in the preceding paper. 4 G. (90%) of *hydrocarbon* (II) were obtained, b. p. 75—78°/10 mm., which after distillation over sodium had $n_D^{15\cdot5^\circ}$ 1·4853, $d_{4^\circ}^{15\cdot5^\circ}$ 0·8769, $[R_L]_D$ 49·10 (calc. for 1 $|^{=}$, 48·13; for 2 $|^{=}$, 49·86) (Found: C, 87·6; H, 12·0. $C_{11}H_{18}$ requires C, 87·9; H, 12·1%). The bromine addition was 292 g. per g.-mol. (calc. for two double bonds, 320), but we do not regard this as trustworthy. A similar dehydration for 2 hours at 140° yielded, after distillation over sodium, 3 g. of mainly dicyclic hydrocarbon, b. p. 82—84°/14 mm., $n_D^{16\cdot5^\circ}$ 1·4903, $d_{4^\circ}^{16\cdot5^\circ}$ 0·8950, $[R_L]_D$ 48·49.

15 G. of 2-methyl-1-$\Delta^{3'}$-butenyl*cyclo*hexanol were heated at 140—150° for 5 hours with 65 c.c. of phosphoric acid (*d* 1·75) and 10 g. of phosphoric oxide. The product, isolated as before and distilled over sodium, had b. p. 84—86°/14 mm., $n_D^{15^\circ}$ 1·4939, $d_{4^\circ}^{15^\circ}$ 0·9053, $[R_L]_D$ 48·22, and was essentially *cis*-9-methyloctalin. Yield, 9 g. (Found: C, 87·8; H, 11·9. Calc. for $C_{11}H_{18}$: C, 87·9; H, 12·1%). 6 G. of the methyloctalin were shaken over-night with 20 g. of potassium permanganate and 7 g. of sodium carbonate in 700 c.c. of water and the acids formed by oxidation were isolated as described in the preceding paper. After crystallisation from very dilute acetic acid, 1·4 g. of an acid, m. p. 156—162°, were obtained which on further crystallisation gave an almost pure acid, m. p. 163—165°, and an inseparable mixture, m. p. 165—175°. The m. p. of the former was not depressed by admixture with the *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid (m. p. 160—163°) described in Part VII. 0·4 G. of the acid of m. p. 163—165° was boiled for an hour with 10 c.c. of methyl alcohol and 1 c.c. of sulphuric acid. The *dimethyl* ester (0·3 g.) was separated in the usual manner, b. p. 122—125°/1 mm. (Found: C, 64·2; H, 8·8. $C_{13}H_{22}O_4$ requires C, 64·4; H, 9·1%). There was no acid fraction. Hydrolysis of the dimethyl ester re-formed an acid of m. p. 161—163°.

2·35 G. of *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid (m. p. 163—165°) were heated with 0·1 g. of baryta to 280—290°. The 8-methyl-2-hydrindanone (1·1 g.) was isolated as before, b. p. 98—100°/12 mm., and rapidly set to a glass. The semicarbazone melted at 218—219° alone and at 220° in admixture with that described in Part VII. The ketone (0·45 g.) when oxidised as before gave 0·3 g. of crude acid, which on crystallisation from water yielded a comparatively insoluble acid, m. p. 170—174°, not depressed on admixture with *cis*-1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid, m. p. 174°.

The residue from the ketonisation to 8-methyl-2-hydrindanone yielded an acid, m. p. 185—190°, which formed radiating clusters of rhombs from dilute acetic acid, m. p. 191—193° alone or mixed with the corresponding acid of Part VII. When this was esterified with methyl-alcoholic sulphuric acid as before, it gave an equal weight of a neutral ester and no acid ester. Hydrolysis of the ester regenerated the original acid, m. p. 193—194°.

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