CCLXXV.—*The Catalytic Hydrogenation of Carone.*

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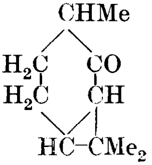
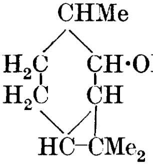
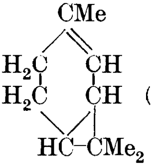
During the course of his researches on the terpenes Baeyer (*Ber.*, 1894, **27**, 1913) prepared the dicyclic ketone carone (I), and until the separation of the two hydrocarbons Δ^3- and Δ^4-carene from the essential oils obtained from *P. longifolia* and *A. Jwarancusa* (J., 1920, **117**, 570; 1922, **122**, 2292) this was the only known substance of the terpene group possessing this dicyclic structure. In view of the probable wide occurrence of these dicyclic hydrocarbons in nature it appeared to us of interest to attempt the synthesis of Δ^4-carene (III). The simplest method available would be the elimination of water from the secondary alcohol (II) which should result from the reduction of carone.

(I.)



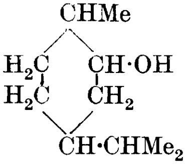


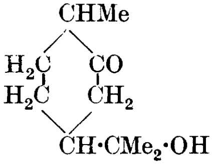
(II.)



(III.)

(IV.)





(V.)

It was shown by Baeyer (*Ber.*, 1895, **28**, 1601) that when carone in moist ethereal solution was reduced with sodium *p*-menthan-2-ol (IV) was produced, whilst treatment of the cyclic ketone with sodium and amyl formate with subsequent decomposition of the hydroxymethylene derivative yielded the corresponding monocyclic ketone. A further indication of the marked instability of the dicyclic system was the fact, also observed by Baeyer (*Ber.*, 1896, **29**, 16), that in the presence of dilute sulphuric acid carone was converted into *p*-menthan-8-ol-2-one (V). It was obvious from these experiments that carone behaved more like an αβ-unsaturated ketone than a dicyclic ketone, but it seemed to us that it might prove possible to hydrogenate it catalytically to the secondary alcohol (II).

Unfortunately, this was found not to be the case. Under the conditions described in the experimental section, after the absorption of 1 mol. of hydrogen, the product consisted mainly of *p*-menthan-2-one mixed with unchanged carone and other substances; on complete reduction (2 mols. of hydrogen), *p*-menthane (in small quantity), *p*-menthan-2-ol (IV), and *l*-*p*-menthane-2 : 8-diol were obtained.

The *p*-menthan-2-ol (IV) obtained was optically inactive and differed in one particular only from the racemic alcohol described by Wallach (*Annalen*, 1893, **277**, 132)—the phenylurethane melted at 107° and not at 75—76°. This discrepancy is in all probability due to the fact that the two alcohols are stereoisomeric, since four racemic forms are possible.

The formation of *l*-*p*-menthane-2 : 8-diol during the hydrogenation is of some interest and it would appear to have been formed by the hydration of the *cyclo*propane ring by the very dilute hydrochloric acid present in the reaction mixture, the hydroxy-ketone subsequently undergoing reduction.

It is somewhat remarkable that no evidence was obtained of the presence of *m*-cymene derivatives, nor does there appear to be any tendency for *cyclo*heptane derivatives to be formed. Although these experiments have not proceeded in the desired direction, they are not without interest since they show quite clearly the great tendency of carone to behave like an αβ-unsaturated ketone. It is proposed to investigate other reactions with carone in order to determine how far this property is general.

EXPERIMENTAL.

The carone required for these experiments was most conveniently prepared in quantity by the method of Kondakov and Gorbanov (*J. pr. Chem.*, 1897, **56**, 256). It had b. p. 150—153°/100 mm., $d_{30^\circ}^{30^\circ}$ 0·9468, $n_D^{30^\circ}$ 1·4739, and $[\alpha]_D^{30^\circ}$ — 250°.

The most satisfactory method of hydrogenation is the following : The ketone (10 g.) was dissolved in acetic acid (20 c.c.), platinic chloride solution (Pt, 10%; 5 c.c.) and gum arabic solution (gum arabic, 2%; 20 c.c.) were added, and the bottle containing the mixture was evacuated and filled with hydrogen. A solution of colloidal palladium (1 c.c.) was added, the apparatus again evacuated, and filled with hydrogen at a pressure of 2 atmospheres. The mixture was mechanically shaken; hydrogen was rapidly absorbed during 2—2½ hours until approximately 2 litres (2 mols.) had been taken up. The mixtures from a number of such experiments were combined and, after separation of the platinum, the oil was taken up with ether, the ether washed with sodium carbonate solution until free from acetic acid, dried, and evaporated. The residual oil partly crystallised on keeping. The solid (A) was collected, and the filtrate distilled under diminished pressure (100 mm.); three main fractions were then obtained, (i) 105—115°, (ii) 135—140°, (iii) 140—180°. The small residue crystallised and was added to (A).

p-*Menthane*.—Fraction (i) was repeatedly distilled over sodium; it then had b. p. 168—169°/685 mm., $d_{30^\circ}^{30^\circ}$ 0·7984, $n_D^{30^\circ}$ 1·435, was optically inactive, had a smell resembling that of light petroleum and was not attacked by warm alkaline permanganate (Found: C, 86·0; H, 13·9. Calc.: C, 85·7; H, 14·3%). The small quantity available did not permit the preparation of crystalline derivatives, but there would appear to be no doubt that the substance is *p*-menthane.

p-*Menthan-2-ol*.—The higher fractions were kept for some days in the ice-box and after removal of the solid deposited (this was added to A), the filtrate was heated with alcoholic potassium hydroxide to hydrolyse any acetyl derivative present. The cyclic alcohol was distilled in steam and then under diminished pressure; b. p. 143—144°/100 mm., $d_{30^\circ}^{30^\circ}$ 0·9004, $n_D^{30^\circ}$ 1·457. It was optically inactive (Found: C, 76·9; H, 12·6. Calc.: C, 76·9; H, 12·8%). The *phenylurethane* crystallised from light petroleum in needles, m. p. 107—108° (Found: N, 5·4. Calc.: N, 5·1%).

The alcohol (10 g.) was oxidised in acetic acid solution with a slight excess of chromic acid; the *p*-menthan-2-one obtained, b. p. 146—148°/100 mm., was identified by means of the oxime, m. p. 105°, and the semicarbazone, m. p. 194—195°, which were compared with authentic specimens.

On oxidation with alkaline permanganate the ketone gave β-*iso*propyladipic acid, which was purified through the calcium salt and recrystallised from water, from which it tended to separate as an oil. The acid was very difficult to purify and melted at 78—80° (Found for the silver salt: Ag, 54·1. Calc.: Ag, 53·7%). Previous workers (Wallach and Koehler, *Annalen*, 1905, **339**, 113; Wallach, *ibid.*, 1906, **343**, 33; 1917, **414**, 287) also have found the acid difficult to crystallise.

l-p-*Menthane-2 : 8-diol.*—The solid (A) crystallised from ethyl acetate in large, glistening prisms, m. p. 155—156°, $[\alpha]_D^{30°}$ − 40° in chloroform (Found : C, 69·7; H, 11·4. Calc. : C, 69·8; H, 11·6%). It was identified with *l*-*p*-menthane-2 : 8-diol (Wallach, *Annalen*, 1917, **414**, 195) (1) by treating it with an acetic acid solution of hydrogen bromide for some days; the solid obtained on addition of water crystallised from methyl alcohol in plates, m. p. 57—58°, and was shown by direct comparison to be terpinene dihydrobromide, (2) by oxidising it in acetic acid with a slight excess of chromic acid; *p*-menthan-8-ol-2-one was obtained, and identified by means of the semicarbazone, m. p. 149° (Found : N, 18·6. Calc. : N, 18·5%).

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[*Received, May* 11*th*, 1926.]