## 1632 SWORD: THE ACTION OF HYDROGEN PEROXIDE ON LIMONENE.

## CCXV.—The Action of Hydrogen Peroxide on Limonene. By JAMES Sword.

THE oxidation of limonene with hydrogen peroxide (2 mols.) in acetic acid solution gives  $\Delta^{8(10)}$ -*p*-menthene-1: 2-diol as the main product, a small yield of terpin hydrate, an aldehyde, etc. Larger quantities of the oxidising agent produce a variety of oxygenated compounds and resinous substances.

Since hydrogen peroxide has no action on hydrocarbons of the terpene series in solvents such as ether, it would appear that acetic acid takes a real part in the reaction, possibly by the formation of peracetic acid. This is supported by the fact that the reaction proceeds more quickly the larger the quantity of solvent used; a certain minimum amount is necessary for the reaction to go to completion in any length of time.

## EXPERIMENTAL.

The limonene used was obtained from oil of bitter orange (J., 1907, 91, 1872) and had b. p.  $175 \cdot 5 - 176 \cdot 5^{\circ}$ ,  $[\alpha]_{D}^{15^{\circ}} + 96 \cdot 89^{\circ}$ ,  $d^{15^{\circ}} 0.8453$ ,  $n^{15^{\circ}} 1.4759$ .

100 C.c. of it in glacial acetic acid (375 c.c.) were shaken continuously for 14-18 days with perhydrol, added gradually (total 180 c.c.). The solution was neutralised with sodium carbonate, and extracted with ether, on occasions up to 40 times. The extract on concentration deposited about 1 g. of terpin hydrate, m. p. 116-117° (in a sealed tube) (Found: C, 62.8; H, 11.5%), and on evaporation left an oil, which was hydrolysed with methyl-alcoholic barium hydroxide, yielding an oil (a). This, on distilling under reduced pressure, gave three fractions : (i) a mobile oil, b. p.  $110-112^{\circ}/10$ mm., (ii) the main fraction, a viscous oil, b. p. 140-143°/10 mm., from which a glycol (b) was isolated, (iii) a semi-vitreous solid, b. p. 150-152°/10 mm. These were all unsaturated, the unsaturation decreasing with increase of boiling point, and gave sodium derivatives [Found : for (i), Na, 9.5; for (ii), Na, 22.7; for (iii), Na, 16.1.  $C_{10}H_{16}(ONa)_2$  requires Na, 21.3%.  $C_{10}H_{17}$ ·ONa requires Na, 13.0%].

By using the residual oil from the preparation of the sodium compounds (only a small quantity of sodium was used for a relatively large amount of oil) the glycol (b) was finally induced to crystallise. Thereafter it could be crystallised directly from (a). The residual oil after its removal yielded a small quantity of a *p*-nitrobenzoate, m. p. 79°, gave with ethereal hydrogen bromide a dihydrobromide which crystallised from ethyl alcohol in pearly plates, m. p. 44–45° (Found : Br, 53.5.  $C_{10}H_{16}$ ,2HBr requires Br, 53.6%), and on distillation with steam yielded an unsaturated oil (Found: C, 72.0; H, 9.9%. 0.1818 G. absorbed 0.165 g. of bromine), from which no nitrobenzoate was obtained, and no solid on hydration.

The glycol (b) is soluble in about 10 parts of water and much more soluble in alcohol or ether. It will crystallise only when hydrated. The hydrate is efflorescent and contains three molecules of water, all of which can be removed over sulphuric acid in a vacuum desiccator in the course of 4—5 days. If dried too rapidly, it liquefies and then sets to a hard, vitreous solid. This, in conjunction with the fact that the hydrate has no definite melting point but begins to melt about 20° below the melting point of the anhydrous substance, indicates that there is an intermediate hydrate of lower melting point. Its solution in alcohol is optically inactive. The anhydrous substance is snow-white, melts sharply at 67.5°, and is clearly the  $\Delta^{g(10)}$ -p-menthene-1: 2-diol described by Prileschaev (*Ber.*, 1909, 42, 4814) (Found : C, 70.6; H, 10.5. Calc., C, 70.6; H, 10.7%).

From the original oxidation products a small quantity of an acid was isolated by means of its silver salt [Found : Ag, 55.4.  $C_6H_{12}(CO_2Ag)_2$  requires Ag, 55.7%.]

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