

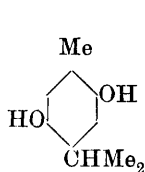
CL.—*Contributions to the Chemistry of the Terpenes.*
Part VII. Synthesis of a Monocyclic Terpene
from Thymol.

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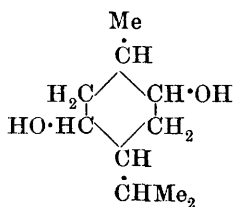
SEVERAL monohydric alcohols of the *cyclohexane* series have already been prepared by the hydrogenation of monohydric phenols in presence of nickel according to Sabatier and Senderens's method, but, so far as we are aware, the reaction has not hitherto been extended to any dihydric phenol. It appeared of interest to investigate the behaviour of a dihydric phenol of the formula $C_{10}H_{12}(OH)_2$ when heated to the requisite temperature with hydrogen in the presence of finely divided nickel, in the hope that it would unite additively with hydrogen and yield a dihydroxymenthane of the formula $C_{10}H_{18}(OH)_2$, and that from this glycol we could obtain a monocyclic terpene, one of the menthadienes, by

elimination of the elements of water. This expectation has been realised. Starting with thymol (3-hydroxycymene), we prepared 6-nitrosothymol (thymoquinoneoxime), reduced this to the corresponding amino-derivative, oxidised the latter to thymoquinone, and by reduction of the thymoquinone with sulphurous acid obtained thymoquinol, $C_{10}H_{12}(OH)_2$. This dihydric phenol was found to be susceptible of direct hydrogenation by the method of Sabatier and Senderens, and gave the desired product, *menthane-2:5-diol*, $C_{10}H_{18}(OH)_2$. Finally, when the glycol so prepared was heated with potassium hydrogen sulphate, it lost the elements of 2 molecules of water, and yielded an unsaturated *hydrocarbon* of the formula $C_{10}H_{16}$, which exhibited the properties of a monocyclic terpene.

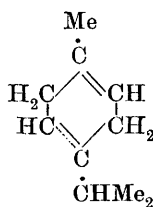
Considering its relationship to thymoquinol (formula I), it is clear that the dihydroxymenthane must have the constitution represented in formula II. The terpene derived from the dihydroxymenthane should contain two ethylenic linkings in the ring, or, in other words, should be isomeric with α -terpinene. Probably it is either $\Delta^{1:4}$ (formula III) or $\Delta^{2:5}$ -menthadiene (formula IV). The quantity of the terpene at our disposal did not permit of experiments being instituted to determine the relative positions of the double bonds, but we hope to be able to examine it more fully later.



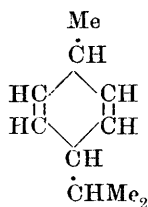
(I.)



(II.)



(III.)



(IV.)

EXPERIMENTAL.

Preparation of Menthane-2:5-diol.—6-Nitrosothymol was obtained by Klages' method (*Ber.*, 1899, **32**, 1518), which gave very satisfactory results. The 6-nitrosothymol was then converted into thymoquinone in the following manner. Twenty-five grams of the nitroso-compound were dissolved in 250 c.c. of 10 per cent. aqueous ammonia, and the solution was saturated with hydrogen sulphide. The precipitate of 6-aminothymol, which separated, was collected, washed with water, and dissolved in 450 c.c. of 3 per cent. sulphuric acid, and to the solution 500 c.c. of water and 250 c.c. of a 10 per cent. solution of potassium dichromate were added. After about half an hour the precipitate which had formed was collected, and dissolved in ten times its weight of glacial acetic acid. Chromic

anhydride was added to this solution in small quantities at a time until the oxidation was completed, and the thymoquinone was then precipitated by addition of water, collected, and dried. The yellow crystals of the quinone melted at 45°.

From the thymoquinone the corresponding quinol was prepared by reduction with sulphurous acid, as described by Carstanjen (*J. pr. Chem.*, 1871, [ii], **3**, 50), and the following method was adopted for its hydrogenation. A long combustion tube, containing finely divided nickel, which was prepared by reducing the pure oxide, in a fine state of division, with hydrogen at as low a temperature as possible, was heated in an air-bath, a porcelain boat containing the substance was placed in the front part, and a fairly rapid current of hydrogen was passed through the tube. The hydrogen, of course, was carefully purified and dried. A number of preliminary experiments had shown that the most favourable temperature for the hydrogenation of the quinol was 190—200°, and accordingly the temperature of the tube was maintained at that point. Under these conditions an extremely viscous liquid slowly distilled from the tube, and was collected in a cooled receiver to which a U-tube filled with glass wool was attached. At first the distillate was quite colourless, but the last portion which passed over had a brown tinge. When the distillate was kept in the ice-chest, crystals began to form, but the process was very slow. The viscous liquid was therefore stirred with a small quantity of benzene, with the result that the greater part of it quickly became crystalline. The crystals were drained from a small proportion of an oily substance with which they were mixed, and recrystallised several times from benzene. The purified product was analysed, and found to be the desired dihydroxymenthane:

0.1262 gave 0.3210 CO₂ and 0.1322 H₂O. C=69.4; H=11.6.

0.1240 „ 0.3160 CO₂ „ 0.1310 H₂O. C=69.5; H=11.7.

C₁₀H₂₀O₂ requires C=69.8; H=11.6 per cent.

Menthane-2: 5-diol, C₁₀H₁₈(OH)₂, crystallises from benzene in very small, colourless plates, which melt at 112°. When dry, it has the form of a white powder, and it has no odour. It is very readily soluble in alcohol, ether, light petroleum, or hot benzene, and readily so in cold benzene. Hot water dissolves it sparingly, cold water scarcely at all. It distils without decomposition under diminished pressure (b. p. about 155°/15 mm.), or in a current of hydrogen at the ordinary pressure.

The small quantity of an oily substance which was separated from the crystalline menthane-2: 5-diol during the process of purification was collected and fractionally distilled under diminished pressure in an atmosphere of dry carbon dioxide. Under 15 mm.

pressure a small fraction distilled at 80—100°, a still smaller fraction at 100—140°, and the bulk at 150—160°. The highest fraction solidified on cooling, and was found to consist almost wholly of menthane-2: 5-diol. The fraction which distilled at 80—100° was too small in quantity to permit of satisfactory purification, but when treated with semicarbazide hydrochloride and potassium acetate in the usual manner it yielded a little of a crystalline solid. When purified by crystallisation from alcohol, in which it is very sparingly soluble, this compound forms small crystals, which are almost colourless, and melt and decompose at 243—244°. It is almost insoluble in water or ether. From an analysis, of which the result is quoted below, it appears not improbable that the compound is the disemicarbazone of a diketone of the formula $C_{10}H_{16}O_2$, derived from the disecundary alcohol, menthane-2: 5-diol:

0.1132 gave 29 c.c. N_2 at 18° and 748 mm. $N = 29.2$.

$C_{12}H_{22}O_2N_6$ requires $N = 29.6$ per cent.

Preparation of a Menthadiene from Menthane-2: 5-diol.—An intimate mixture of menthane-2: 5-diol with twice its weight of dry powdered potassium hydrogen sulphate was placed in a flask attached to a reflux condenser, and heated in a bath of fusible metal. When the temperature of the bath approached 190° a vigorous reaction began, and a colourless liquid vaporised and condensed in the tube. After having been heated for about half an hour at 190—200°, the mixture was cooled and distilled in a current of steam. A mobile, colourless liquid distilled with the steam and floated on the surface of the water in the receiver. The liquid was extracted with ether, the ethereal solution dried, the ether removed by distillation, and the residual liquid again mixed with potassium hydrogen sulphate and heated as before. The resulting mixture was distilled in a current of steam, the liquid extracted from the distillate with ether, the ethereal solution dried, and the ether distilled off. The liquid remaining in the flask was repeatedly distilled over sodium until no sign of any reaction could be observed, and finally we obtained a small quantity of a substance of practically constant boiling point, which analysis showed to have the composition of a terpene:

0.1540 gave 0.4963 CO_2 and 0.1636 H_2O . $C = 87.9$; $H = 11.8$.

0.2897 „ 0.9358 CO_2 „ 0.3024 H_2O . $C = 88.1$; $H = 11.6$.

$C_{10}H_{16}$ requires $C = 88.2$; $H = 11.8$ per cent.

The *terpene* thus obtained is, as already stated, probably one of the isomeric terpinenes not hitherto described. It is colourless, has a rather faint odour somewhat like that of limonene, and a characteristic burning taste like oil of turpentine. Its boiling point is 179°/760 mm.; $n_D^{20} = 1.4779$; the specific gravity is somewhat

greater than 0.84, but the quantity of the substance available was too small for an exact determination, especially as it appears to polymerise on keeping. It is practically insoluble in water, but dissolves in the usual organic solvents. It at once decolorises a dilute alkaline solution of potassium permanganate. When mixed with a solution of dry bromine in dry chloroform, it instantly unites with the bromine to form an additive compound, but the product must be unstable under the conditions of the experiment, since when rather more than three atomic proportions of bromine had been added, evolution of hydrogen bromide began. When treated with nitrous acid according to Wallach's method, the liquid turns yellow, but no crystalline nitrosite could be isolated. We hope to be able to complete the examination of this terpene before long.

It is our intention to endeavour to obtain terpenes from other monohydric phenols isomeric with thymol on the lines indicated in this paper.

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