396. *Researches on Phellandrenes. Part IV. A Comparison of the Catalytic Dehydrogenation of* l-α-*Phellandrene and* l-*Piperitone.*

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Earlier investigations have shown that hydrogenating catalysts may simultaneously hydrogenate *l*-piperitone to *d-iso*menthone, etc., and dehydrogenate it to thymol (J., 1923, **123**, 2916; 1929, 2068; *Chem. Reviews*, 1930, **7**, 20). It has thus been pointed out that "the hydrogenation of piperitone is a reversible process and that an optimum temperature exists for any specific set of conditions; above this temperature dehydrogenation is accelerated in conformity with the general principle of Sabatier and Senderens" (J., 1929, 2069). The yields of thymol obtained in these experiments were small, but Treibs and Schmidt (*Ber.*, 1927, **60**, 2335), by passing vaporised piperitone over a nickel catalyst at 280°, obtained a product containing 45% of thymol and 32% of menthone.

We show below that, although piperitone was practically unaffected by platinised asbestos or ordinary platinised or palladised charcoal at 300°, it was converted almost quantitatively into thymol by treatment with Zelinski's platinised charcoal catalyst in an atmosphere of carbon dioxide at 300°. Rupe's porcelain–nickel catalyst similarly afforded a yield of more than 70% of thymol at 250°; but at the ordinary temperature in an atmosphere of hydrogen the same catalyst effected a practically quantitative hydrogenation of piperitone to menthones. These interesting results may be reconciled with the view (J., 1929, 2070) that a partial hydrogenation of piperitone is an essential prelude to its dehydrogenation, since all the catalysts employed were activated with hydrogen.

A noteworthy example of simultaneous hydrogenation and dehydrogenation is provided by *l*-α-phellandrene. When heated in an atmosphere of carbon dioxide with an activated nickel catalyst, this terpene yielded a mixture of *p*-cymene and *p*-menthane, in the approximate proportion of 4 parts to 1. Here, part of the hydrogen resulting from the dehydrogenation is made available for hydrogenation, the equilibrium being dependent upon the conditions of the reaction. A close parallel thus exists in this respect between α-phellandrene and piperitone. A very similar example is provided by *d*-limonene, which in presence of palladised asbestos at 180—185° was found by Zelinski (*Ber.*, 1924, **57**, 2058) to undergo transformation into an optically inactive mixture of *p*-cymene and *p*-menthane, in which the former predominated.

EXPERIMENTAL.

Catalytic Dehydrogenation of Piperitone.—(1) The second form of circulatory apparatus devised by Read and Robertson (*J. Soc. Chem. Ind.*, 1929, **48**, 263T) was used in various experiments, circulation being maintained by means of a slow current of carbon dioxide. In each case the catalyst was submitted to a preliminary heating *in situ* at 300° in a slow stream of pure dry hydrogen, until no more moisture was expelled. In one experiment, the quartz U-tube was loosely packed with 5% platinised asbestos, kept in position with plugs of asbestos fibre: when freshly distilled *l*-piperitone was circulated at 300° for 4 hours, no appreciable dehydrogenation occurred. In other experiments, an ordinary palladised charcoal catalyst and also a 30% platinised charcoal catalyst (*J. Soc. Chem. Ind.*, 1936, **55**, 347T) produced no appreciable dehydrogenative effect on *l*-piperitone under similar conditions.

(2) Zelinski's platinised charcoal catalyst (*Ber.*, 1926, **59**, 2591) was packed in the silica tube of a vertical furnace of special design (*J. Soc. Chem. Ind.*, 1936, **55**, 347T) and activated in dry hydrogen at 200°. Dry carbon dioxide was then passed through the apparatus, the temperature being raised meanwhile to 300°. When *l*-piperitone was passed over the catalyst at the rate of one drop per minute, the colourless liquid collecting in the receiver consisted of almost pure thymol, only a very small proportion of unchanged piperitone being recoverable from it. The same specimen of catalyst could be used repeatedly in effecting this dehydrogenation.

(3) A mixture of *l*-piperitone (20 g.) and Rupe's porcelain–nickel catalyst (20 g.) (*Ber.*, 1916, **49**, 55) was heated in a current of dry carbon dioxide for 8 hours at 240—250° in a flask provided with an air condenser. Extraction with alkali showed that the product contained about 62% of thymol, the remainder being *dl*-piperitone. The same specimen of catalyst when heated for a longer time with a fresh sample of piperitone effected a 72% conversion into thymol.

Rupe's catalyst was shown to bring about hydrogenation of piperitone under the following conditions. A mixture of *l*-piperitone (40 g.), $\alpha_{D}^{16^{\circ}}$ − 42·0° (*l* 1), catalyst (40 g.), rectified spirit (100 c.c.), and water (100 c.c.) was shaken in a hydrogenating bottle with hydrogen under a pressure of 50 lb./sq. in. After 2½ hours the catalyst was removed by filtration and washed with ether. The ether washings were used to extract the filtrate. The extract was washed well with water, dried, and distilled from the water-bath. The residue (40 g.) consisted of crude *d-iso*menthone, having α_{D} + 53·0° (*l* 1). The same sample of catalyst was used successfully in six similar hydrogenations. A portion (171 g.) of the product when distilled gave a fraction (153 g.) having b. p. 84—87°/10·5 mm., $\alpha_{D}^{16^{\circ}}$ + 57·3° (*l* 1) (compare J., 1923, **123**, 2922).

Catalytic Dehydrogenation of l-α-Phellandrene.—*l*-α-Phellandrene obtained from the essential oil of *E. dives* by fractional distillation had b. p. 57—58°/10 mm., $n_{D}^{15^{\circ}}$ 1·4780, $\alpha_{D}^{15^{\circ}}$ − 67·3° (*l* 1). The terpene (30 g.) was mixed with an activated nickel catalyst (10 g.) in a flask with an air condenser, the operation being carried out in an atmosphere of dry carbon dioxide. Heat was evolved so rapidly that the liquid began to boil, and more cold *l*-α-phellandrene was added quickly to reduce the temperature. Later, the mixture was kept at 150° in a metal-bath for 10 hours, a slow stream of carbon dioxide being passed through the apparatus meanwhile.

The filtered liquid had $n_{\mathrm{D}}^{15^\circ}$ 1·4782, and was optically inactive; its odour resembled that of *p*-cymene, and the absence of phellandrene was indicated by its failure to yield a nitrosite (J., 1923, **123**, 1663). The product distilled almost completely at 56—60°/10 mm., and the physical constants of the distillate ($d_{4^\circ}^{15^\circ}$ 0·844, $n_{\mathrm{D}}^{13^\circ}$ 1·4813) corresponded approximately to those of a mixture of *p*-cymene (4 parts) and *p*-menthane (1 part).

Part of the distillate (20 g.) was nitrated by the gradual addition, at 20—25° with mechanical stirring, of a mixture of concentrated nitric (7·2 c.c.) and sulphuric (8·2 c.c.) acids, the temperature being ultimately raised to 40° (compare Söderbaum and Widman, *Ber.*, 1888, **21**, 2126). The product when isolated in the usual way yielded two fractions upon distillation: (1) a colourless liquid (13 g.), b. p. 58—61°/12 mm., $n_{\mathrm{D}}^{14^\circ}$ 1·4747; (2) a lemon-yellow liquid (5 g.), b. p. 134°/12 mm., $n_{\mathrm{D}}^{14^\circ}$ 1·5332. Fraction (1), when renitrated twice, yielded more (2·1 g.) of fraction (2), together with a fraction (3), b. p. 58°/12 mm., $n_{\mathrm{D}}^{15^\circ}$ 1·4381. The last fraction consisted of *p*-menthane (compare Konowaloff, *J. Russ. Phys. Chem. Soc.*, 1899, **31**, 1027; 1904, **36**, 237) (Found: C, 85·3; H, 14·2. Calc.: C, 85·6; H, 14·3%). A specimen of *p*-cymene when nitrated under the above conditions gave a product, b. p. 135°/12 mm., $n_{\mathrm{D}}^{13^\circ}$ 1·5335, which was substantially identical with fraction (2) above. Confirmation of the presence of *p*-cymene in the product of dehydrogenation of *l*-α-phellandrene was afforded by a study of absorption curves, for which we are indebted to Mr. R. E. Lishmund, B.Sc., of the Department of Natural Philosophy, United College, University of St. Andrews. The positions of the heads of absorption bands and the molecular extinction coefficients were as follows: product of hydrogenation, 2725 A., 548 and 2650 A., 482; *p*-cymene, 2725 A., 588 and 2640 A., 504. The observations were made for alcoholic solutions.

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