

CLXIV.—*The Conversion of Pinene into Sobrerol.*

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As stated in a former communication, sobrerol can be obtained by oxidising pinene with aqueous mercuric acetate in the cold (Henderson and Agnew, *Trans.*, 1909, 95, 289). The pinene used for the experiments quoted in that paper showed only a small degree of optical activity, and, naturally, it was the inactive modification of sobrerol that was produced, the mixture of *d*- and *l*-pinene yielding an optically inactive mixture of *d*- and *l*-sobrerol. At the suggestion of Professor Pope, we have now examined the behaviour of *d*- and *l*-pinene towards mercuric acetate.

The *d*-pinene, obtained from Burmese oil of turpentine, was distilled in a current of steam, dried over potassium hydroxide, and fractionated with the aid of a "pear" fractionating column. The portion which distilled at 155–157° was used for oxidation; it was found to have  $d_{4}^{20}$  0.8599 and  $[\alpha]_{D}^{20}$  34.1°. The *l*-pinene was obtained from French oil of turpentine, and purified in a similar manner. The portion used for oxidation distilled at 156°; it was found to have  $d_{4}^{20}$  0.8606 and  $[\alpha]_{D}^{20}$  –39.2°. Fifty grams of each specimen were oxidised with 350 grams of mercuric acetate dissolved in 1500 c.c. of water. After agitation for several days, the solutions were filtered, and the filtrates thoroughly extracted with chloroform. The chloroform extracts, after being washed with aqueous sodium carbonate and dried over anhydrous potassium carbonate, were heated until the chloroform was expelled, and there remained viscous, brown residues, which solidified on standing, and were purified by repeated crystallisations from benzene. In each case the product obtained was the inactive modification of sobrerol melting at 131°; in alcoholic solution, neither product exhibited any optical activity. Another specimen of pinene from American oil of turpentine, much more strongly dextrorotatory ( $d_{4}^{20}$  0.8609,  $[\alpha]_{D}^{20}$  13.9°) than that used in our former experiments, was also oxidised with mercuric acetate, and yielded again inactive sobrerol.

It is therefore clear that optical inversion occurs when *d*- or *l*-pinene is converted into sobrerol by the mercuric acetate method as described. However, the formation of sobrerol by this method is apparently not a case of simple oxidation of pinene. In all probability the first step in the process is the formation of an additive compound of pinene and mercuric acetate, which, under the conditions of the experiment, undergoes a subsequent change into sobrerol.

The comparative ease with which sobrerol can be obtained by means of mercuric acetate suggested the application of that reagent to test for the presence of pinene in Russian and in Swedish oil of turpentine. A specimen of the Russian oil was washed with aqueous sodium carbonate, distilled with steam, dried over potassium hydroxide, and fractionated with a "pear" column. A small fraction distilled at 156—157°, but the bulk of the oil had a higher boiling point. This fraction was found to have  $d_{40}^{20}$  0.8598 and  $[\alpha]_D^{20}$  28.4°, and on treatment with mercuric acetate by the method described above it gave a satisfactory yield of inactive sobrerol; hence the specimen of Russian oil of turpentine undoubtedly contained a small proportion of *d*-pinene.

A sample of Swedish oil of turpentine was purified in a similar manner, and on distillation yielded a fairly large fraction boiling below 150° and a very small fraction boiling at 154—157°, while the bulk of the oil had a higher boiling point. The fraction which distilled at 154—157° was taken for oxidation; it was found to have  $d_{40}^{20}$  0.7834 and  $[\alpha]_D^{20}$  5.7°. It did not react with mercuric acetate nearly so easily as the specimens of pinene, and only a small quantity of an oxidation product was extracted by chloroform. This product appeared to contain no sobrerol, and we therefore conclude that the Swedish oil of turpentine contained no pinene, or, at the most, an exceedingly small proportion.

We take this opportunity of expressing our thanks to Professor Pope for kindly supplying us with several specimens of pinene from different sources.

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