CCCCIX.—*The Oxidation of Dipinene.*

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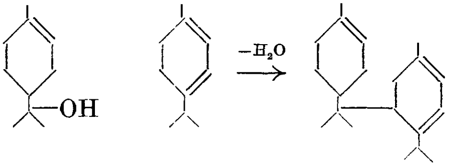
THE methods which have been employed for the conversion of mono- and di-cyclic terpenes and their derivatives into diterpenes have been reviewed by Kondakov and Saprikin (*Bull. Soc. chim.*, 1925, **37**, 918, 1045. See also Carter, Read, and Smith, *J. Soc. Chem. Ind.*, 1925, **44**, 543T). No definite crystalline addition compounds have been obtained from these synthetic diterpenes, and it is suggested in the communications mentioned above that this is due to the presence of various isomeric diterpenes.

Kondakov and Saprikin suggested that the diterpenes obtained from pinene by the action of various polymerising agents (sulphuric acid, ferric chloride, fuller's earth, etc.) contain two six-membered rings united through a *gem*-dimethyl group, and that *cyclo*propane and *cyclo*butane rings are probably also present. Carter, Read, and Smith, on the other hand, suggested that the diterpenes which they obtained by the action of phosphoric acid on pinene, limonene, and cineole were possibly formed owing to the production and subsequent condensation of terpinene and terpineol. The terpineol residue might become attached to position 5, 6, 7, or 8 in the terpinene molecule :



No well-characterised oxidation products have hitherto been obtained from any of the diterpenes produced by the polymerisation of mono- and di-cyclic terpenes. By applying the method of " dehydrogenating disruption " with manganese dioxide and sulphuric acid, developed by Ruzicka, to a dipinene produced by the action of hydrogen chloride and ferric chloride upon pinene, we have obtained an oxidation product from which trimellitic, terephthalic, and benzoic acids were isolated. This result supports the suggestion that diterpenes of this type contain two hexagonal nuclei united through a chain of one or two carbon atoms. Further deductions would, however, be unwarranted, because it is now well known (Carius, *Annalen*, 1868, **148**, 50; Ruzicka and Rudolph, *Helv. Chim. Acta*, 1927, **10**, 917) that some of the benzenecarboxylic acids obtained by oxidation with manganese dioxide and sulphuric acid are not produced normally from the carbon framework of the oxidised substance, but contain adventitious carboxyl groups.

EXPERIMENTAL.

Preparation of Dipinene.—Moist hydrogen chloride was passed into a mixture of 300 g. of pinene (b. p. 155—160°; $[\alpha]^{16°}_{5770}$ − 24·4°) with light petroleum (250 c.c.) until 87 g. had been absorbed. After another 300 g. of pinene had been added, anhydrous ferric chloride (30 g.) was introduced in small portions with stirring. This caused the solution to boil, and, after it had cooled, it was washed with sodium hydroxide and water and dried over sodium sulphate. The solvent was then removed and the residue distilled in a vacuum. The diterpene fraction was repeatedly distilled, finally over sodium, through a 10 cm. Vigreux column and 77 g. of a colourless oil were ultimately obtained, b. p. 183—184°/15 mm., $d^{20°}_{4°}$ 0·9260, $n^{20°}_{D}$ 1·5174, $[R_L]_D$ 88·92 (calc. for a dicyclic diterpene, 88·76).

Oxidation of Dipinene.—A preliminary experiment showed that the physical constants were only very slightly changed when dipinene was boiled with 57% sulphuric acid for 36 hours.

Powdered manganese dioxide (370 g. of 82%) was added in small portions during ½ hour to a mixture of dipinene (22 g.), concentrated sulphuric acid (500 c.c.), and water (600 c.c.). After the mixture had been refluxed for 2½ days, manganese dioxide (100 g.) and concentrated sulphuric acid (175 c.c.) were added and the boiling was continued until solution of the oil was complete (1 day). The product was diluted with an equal volume of water and filtered while still warm. The residual manganese dioxide was digested at 100° with dilute sodium hydroxide solution, the filtered alkaline liquid added to the acid filtrate, and the whole exhaustively extracted with alcohol-free ether. The dark brown product (approx. 6 g.) obtained was dissolved in dilute ammonia, filtered from a small quantity of gelatinous material, neutralised, and precipitated with silver nitrate. The silver salts, after being dried at 60° in a vacuum for 24 hours, were mixed with dry methyl iodide (7 g.) and absolute ether (10 c.c.), and the mixture, which became warm, was finally heated under reflux (3 hours) to complete the reaction. The product was diluted with ether, filtered, extracted with dilute sodium hydroxide solution, washed with water, and dried. (The alkaline layer contained an insignificant amount of organic material.) The residue obtained by removal of the ether was distilled in a vacuum and the following fractions were collected: (1) b. p. 50—60°/5 mm. (1·1 g.), (2) 70—80°/0·2 mm. (1·1 g.), (3) 80—140°/0·2 mm. (0·6 g.), (4) 140—150°/0·2 mm. (2·4 g.).

Fraction (1) was hydrolysed by alcoholic potassium hydroxide and yielded benzoic acid, m. p. 119—121° (Found for the silver salt: Ag, 47·3. Calc.: Ag, 47·1%) (*p*-nitrobenzyl ester, m. p. 88—89°).

Fraction (2) was recrystallised three times from hot methyl alcohol and then melted at 137—138° (methyl terephthalate melts at 140°). The acid obtained by hydrolysis sublimed without melting and was identified with terephthalic acid by analysis of the silver salt (Found: Ag, 56·5. Calc.: Ag, 56·8%) and by conversion into the *p*-nitrobenzyl ester, m. p. 263·5°.

Fraction (3) was recrystallised from methyl alcohol, but no homogeneous substance could be isolated.

Fraction (4) was only partly saponified by alcoholic potassium hydroxide and was therefore hydrolysed by heating at 150° for 8 hours with concentrated hydrochloric acid (4 parts) (compare Ruzicka, Schinz, and Meyer, *Helv. Chim. Acta*, 1923, 6, 1091). The resulting acid was repeatedly crystallised from acetone–benzene and melted at 224°. Analysis of the silver salt (Found: Ag, 61·3. Calc. for $C_9H_3O_6Ag_3$: Ag, 61·0%) indicated that the acid was one of the benzenetricarboxylic acids. Of these, hemimellitic acid is eliminated by its melting point (190°), and trimesic acid (m. p. 380°) by the fact that the acid obtained from dipinene gave a fluorescent product on condensation with resorcinol. Somewhat discordant values, ranging from 216—218° (Schultz, *Annalen*, 1908, **359**, 129;

Aschan and Virtanen, *ibid.*, 1921, **424**, 213) to 230° (von Braun, Kirschbaum, and Schuhmann, *Ber.*, 1920, **53**, 1164), have been given as the melting point of trimellitic acid.

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