159. *Oxidation of* [2 : 2 : 1]bicyclo*Heptene*-2 (*Norbornylene*).

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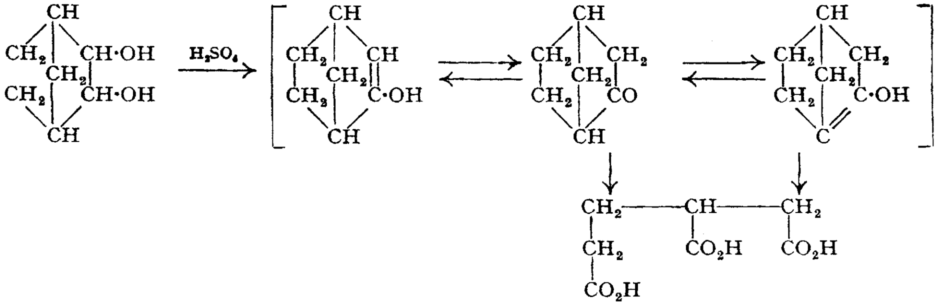
The preparation of *cyclo*pentane-*cis*-1 : 3-dicarboxylic acid is readily effected by oxidation of norbornylene with aqueous sodium permanganate, the pH of the reaction being controlled by the continuous passage of carbon dioxide through the reaction mixture during the permanganate addition. This method of oxidation may be applicable to other olefins and unsaturated compounds. The end-point of the reaction appears to be very sharp, and it is even possible that certain unsaturated compounds could be determined in this way.

The oxidation of norbornylene in glacial acetic acid solution with hydrogen peroxide yields a glycol, but further oxidation of this with chromic acid gives, not *cyclo*pentanedicarboxylic acid, but butane-1 : 2 : 4-tricarboxylic acid, indicating that some rearrangement occurs. This reaction was, however, not further investigated.

In the course of work on the synthesis of substituted *cyclo*pentanes, it became desirable to prepare *cyclo*pentane-*cis*-1 : 3-dicarboxylic acid in a quantity of several kilograms. The method of preparation used by Pospischill (*Ber.*, 1898, **31**, 1950) and later by Perkin and Scarborough (*J.*, 1921, **119**, 1405) was briefly investigated but was so obviously unsuitable for the production of appreciable quantities of the acid that search was made for a simpler alternative.

The straightforward oxidation of [2 : 2 : 1]*bicyclo*heptene-2 (norbornylene) should yield the desired acid, since the carbon atoms in the unsaturated bridge must lie in a *cis*-position in relation to the remaining *cyclo*pentane ring. Norbornylene can be readily prepared in quantity by condensing *cyclo*pentadiene with ethylene according to the method of Joshel and Butz (*J. Amer. Chem. Soc.*, 1941, **63**, 3350).

Oxidation of norbornylene in glacial acetic acid with 30% hydrogen peroxide in the normal way was found to give a mixture of the *glycol* and its monoacetate. Further, oxidation of this mixture with chromic–sulphuric acid (Bennett and Gudgeon, *J.*, 1938, 1679) gave a mixture of acids which, when esterified and fractionated under reduced pressure, contained no detectable quantity of the required ester. The main component was identified as butane-1 : 2 : 4-tricarboxylic acid by conversion into *cyclo*pentanone-3-carboxylic acid according to the method given by Kay and Perkin (*J.*, 1906, **89**, 1643) and Haworth and Perkin (*J.*, 1908, **93**, 575). Some rearrangement must, therefore, have taken place, probably by the action of the sulphuric acid present on the glycol:



The above scheme is merely a suggested method of rearrangement. No investigation of the mechanism of the reaction was carried out.

Direct oxidation of norbornylene in *iso*octane solution with potassium permanganate, however, gave the required acid in low yield. The volume of solution to be worked up at the end of the oxidation was considerable owing to the relatively low solubility of potassium permanganate, and it was obvious that, unless the method could be improved, the preparation of the required acid in quantity would be extremely tedious and time-consuming. Further, the yield varied considerably in repeat experiments carried out under apparently identical conditions.

Search was therefore made for a method in which the reaction conditions could be more accurately controlled. Control of the temperature and of the pH of the reactants appeared to be possible methods of directing the course of the oxidation and improving the yield of the required acid. The use of the more soluble sodium permanganate in place of the potassium salt should minimise the volume of solution to be handled at the end of the experiment.

An experiment was therefore carried out in which norbornylene was oxidised in *iso*octane solution with aqueous sodium permanganate at 5—10°. It was found that the colour of permanganate persisted after the addition of approximately the theoretical amount. This had not been observed in any of the previous work. The crude acid was semi-solid and was much cleaner than that obtained previously. The yield was 65%.

Eventually, it was found that an excellent yield of clean product could be obtained by carrying out the oxidation with sodium permanganate and controlling the pH of the reaction mixture by passing a stream of carbon dioxide through it during the permanganate addition. Control of the temperature to 5—10° was found to be unnecessary, but it was not allowed to rise above 50°. The end of the reaction was indicated by the presence of excess permanganate in the mixture. The crude acid was pale yellow, immediately crystallisable, and was consistently obtained in good yield (95%).

EXPERIMENTAL.

(a) *Oxidation of Norbornylene with Hydrogen Peroxide and Chromic Acid.*—Norbornylene (47 g.) was dissolved in glacial acetic acid (1000 ml.), and hydrogen peroxide (100-vol., 268 ml.) added with stirring. A slight reprecipitation of norbornylene occurred, but this redissolved on standing for 48 hours at room temperature. The product was steam-distilled to remove most of the acetic acid, and concentrated under reduced pressure to about 300 ml. Sodium bicarbonate was then added until no further effervescence occurred, and the solution was extracted continuously with ether. The product distilled between 140° and 150°/19 mm., and the higher-boiling portion tended to crystallise. Some of this solid was separated and recrystallised, first from benzene–light petroleum, then twice from di*iso*propyl ether. It then melted at 185—185·5° (corr.) with some decomposition.

Analysis of the liquid portion of the distillate indicated that it might be a mixture of the glycol and its monoacetate. A portion was refluxed with potassium hydroxide solution and the solid glycol was extracted from the dark product with carbon tetrachloride. The solid was therefore probably 2 : 3-*dihydroxy*-[2 : 2 : 1]bicyclo*heptane* (trans-?) (Found : C, 65·8; H, 9·6. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%). This product was not isolated in normal runs, but was oxidised further with chromic acid. The crude mixed acids were extracted continuously and converted into the ethyl esters.

From 330 g. of norbornylene, 284 g. of mixed esters were obtained. These were then fractionated under reduced pressure in a small column of about 40 theoretical plates, and were found to contain 173 g. of a product which boiled steadily at 162°/6 mm. The only other component identified was ethyl succinate; there was no detectable quantity of *cyclo*pentanedicarboxylic ester.

The acid obtained from the high-boiling ester could be crystallised from acetone–light petroleum, and after two such crystallisations melted at 119·3—119·9° (corr.) after thorough drying in a vacuum oven [Found : C, 44·5; H, 5·3; equiv., by titration with baryta, 63·0. Calc. for $C_4H_7(CO_2H)_3$: C, 44·2; H, 5·3%; equiv., 63·4]. The triethyl ester had b. p. 162°/6 mm., $n_D^{20°}$ 1·4390, $d_{4°}^{20°}$ 1·0755 [Found : C, 57·1; H, 8·1; *M* (micro-Rast), 268. Calc. for $C_{13}H_{22}O_6$: C, 56·9; H, 8·1%; *M*, 274·4]. 13·7 G. of the ester were subjected to the Dieckmann condensation as described by Kay and Perkin (*loc. cit.*) (see also Haworth and Perkin, *loc. cit.*), and ethyl *cyclo*pentanone-2 : 3-dicarboxylate (6·5 g.) was obtained, b. p. 108°/0·9 mm., $n_D^{20°}$ 1·4574; it gave an intense crimson colour with ferric chloride (Found : C, 58·3; H, 7·4. Calc. for $C_{11}H_{16}O_5$: C, 57·9; H, 7·1%).

Acid hydrolysis of this ester (5 g.) gave *cyclo*pentanone-3-carboxylic acid (2·5 g.) which, after two crystallisations from di*iso*propyl ether, melted at 61·0—62·0° (corr.) (Found : C, 56·4; H, 6·3. Calc. for $C_6H_8O_3$: C, 56·2; H, 6·3%).

The oxime was prepared, but decomposed above 160° with charring but without melting.

(b) *Oxidation of Norbornylene to* cis-cyclo*Pentane*-1 : 3-*dicarboxylic Acid.*—Norbornylene (100 g.) was dissolved in *iso*octane (200 ml.), and the solution was added to 3 l. of water in a 10-l. flask fitted with a tap-funnel, thermometer, bell stirrer, and carbon dioxide inlet tube. A steady stream of carbon dioxide was passed in while a 15% solution of sodium permanganate was added with vigorous stirring at such a rate that the temperature did not rise above 50°. When the reaction was complete the colour of permanganate persisted even on prolonged stirring. About 3480 g. of the permanganate solution were required, and the addition took about 4 hours. Sulphur dioxide was then passed in to remove manganese dioxide, and the *iso*octane was recovered for re-use by steam distillation. The clear, pale pink solution was concentrated to about 2 l., acidified with sulphuric acid (500 g.) in water (700 g.), and extracted with three portions of ether (3 × 500 ml.). On removal of ether from the combined extract, 130 g. of pale yellow acid remained, m. p. 109—111°.

Continuous extraction of the remaining aqueous solution with ether yielded a further 25—30 g. of acid; this was often dark, owing possibly to further oxidation by traces of nitrate present in the permanganate, since red fumes were sometimes observed. After one recrystallisation from benzene, 115 g. of acid, m. p. 116°, were obtained; the chief impurity was probably the anhydride, since the benzene solution was refluxed for 2 hours in an apparatus for the removal of water, which continued to be formed in small quantity. A further recrystallisation from water, in which the acid is very soluble, raised the m. p. to 119·9—120·6° (corr.), unaffected by repeated recrystallisations from water (Found: C, 53·6; H, 6·7. Calc. for $C_7H_{10}O_4$: C, 53·2; H, 6·4%). The ethyl ester had b. p. 146°/20 mm., $n_D^{20°}$ 1·4474, $d_{4°}^{20°}$ 1·0574 (Found: C, 61·7; H, 8·4. Calc. for $C_{11}H_{18}O_4$: C, 61·7; H, 8·5%).

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