287. *A Synthesis of Homocaronic Acid.*

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FROM amongst the oxidation products of *d*-Δ^3-carene, Simonsen and Rau (J., 1923, **123**, 556) isolated an acid, $C_8H_{12}O_4$, m. p. 136—137°, which they regarded as *cis*-homocaronic acid (II), although contrary to expectation it was somewhat readily attacked by potassium permanganate in alkaline solution and did not yield terpenylic acid on ring fission. Previous attempts (Hariharan, Menon, and Simonsen, J., 1928, 434; Menon and Simonsen, J., 1929, 303) to synthesise an acid of this constitution were unsuccessful, but we have now prepared the *cis*- and the *trans*-modification of the cyclic acid by a method analogous to that used in the synthesis of the higher homologues, *cis*- and *trans*-3-carboxy-1 : 1-dimethyl*cyclo*propane-2-propionic acids (J., 1932, 1424).

Ethyl Δ^{β}-*iso*hexenoate (I) (Boxer and Linstead, J., 1931, 740; Linstead, J., 1932, 115*)

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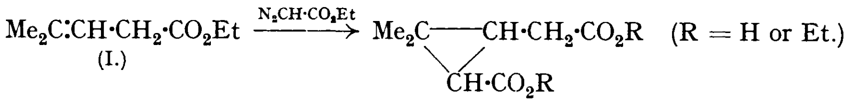
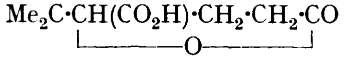
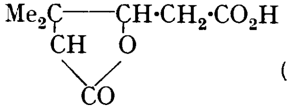
* We are greatly indebted to Dr. R. P. Linstead for very complete details of the most satisfactory method for the preparation of this ester.

condensed readily with ethyl diazoacetate in the presence of copper–bronze to give a mixture of the esters of *cis*- and *trans*-homocaronic acids (II) and *cyclo*butane-1 : 2 : 3 : 4-tetracarboxylic acid. After hydrolysis with methyl-alcoholic potassium hydroxide, the


(I.) (II.)


(III.)


(IV.)

acids were separated as described below. *cis*-Homocaronic acid, m. p. 135—136°, was found by direct comparison to be identical in all respects with the acid obtained by the oxidation of *d*-Δ^3-carene. In agreement with the previous observations, the acid was somewhat readily attacked by potassium permanganate in alkaline solution, and on treatment with hydrochloric acid at 100° it did not yield terpenylic acid, but gave a lactone, m. p. 101—102°, which, if no molecular rearrangement has occurred, must be either (III) or (IV). The constitution of the lactone was not determined since it could not be reduced with hydriodic acid or with sodium amalgam, resembling in this respect the lactones described by Conrad and Gast (*Ber.*, 1899, **32**, 145) and by Perkin and Thorpe (J., 1913, **103**, 1762). An attempt to condense ethyl Δ^{α}-*iso*hexenoate with ethyl diazoacetate was unsuccessful.

EXPERIMENTAL.

Condensation of Ethyl Δ^{β}-iso*Hexenoate and Ethyl Diazoacetate.*—To ethyl Δ^{β}-*iso*hexenoate (10 g.) with copper–bronze (0·5 g.) in suspension, ethyl diazoacetate (8 g.) was added gradually, the temperature being maintained at 45—50°; the condensation proceeded smoothly with evolution of nitrogen. The products of six reactions were combined, filtered from copper–bronze, and systematically fractionated (twice) under diminished pressure (16 mm.), the following fractions being obtained: (i) 72—80° (14 g.), (ii) 80—110° (7 g.), (iii) 110—122° (3 g.), and (iv) 122—137° (21 g.). The fractions distilling below 120°/16 mm. (46 g.) were combined and treated again with ethyl diazoacetate (37 g.) in the presence of copper–bronze (2 g.) and the reaction product fractionated as before; the main fraction (iv*a*) had b. p. 123—136°/15 mm. (23 g.).

Fraction (iv) was digested with potassium hydroxide (17 g.) in methyl alcohol (90 c.c.) for 3 hours, whereupon a sparingly soluble potassium salt (*A*) separated. The cooled solution was filtered, and the filtrate after addition of water evaporated on the water-bath in a current of carbon dioxide. The aqueous solution was acidified with phosphoric acid, a solid acid being deposited. This was dissolved in ethyl acetate, the solution extracted (7 times) with the same solvent, the combined extracts dried (magnesium sulphate), and the solvent evaporated. The residue (14·7 g.) solidified, and after crystallisation from water had m. p. 120—167°, not improved by crystallisation from water or toluene. A mixture of acids having similar properties was obtained by the hydrolysis of (iii) and (iv*a*).

For the isolation of *cis*-homocaronic acid, the crude acid (3 g.) was mixed with acetic anhydride (10 c.c.) and heated in a sealed tube at 220° for 4 hours. The excess of anhydride was removed by distillation, and the residual oil then had b. p. 155—160°/17 mm. The liquid anhydride was dissolved in hot water, and on cooling, the *cis*-acid separated in rosettes of needles, m. p. 135—136° (sintering 115°), recrystallised from water, m. p. 135—136° (sintering 125°). This m. p. was unchanged on admixture with *cis*-homocaronic acid prepared from *d*-Δ^3-carene (Found: C, 55·6; H, 7·2; *M*, 172·9. Calc. for $C_8H_{12}O_4$: C, 55·8; H, 7·0%; *M*, 172).

For the preparation of the *trans*-acid, the crude acid (see above) was digested with dry ether; a portion remained undissolved and a further quantity of the same acid was deposited from the ether on standing. The fractions (m. p. 189—190°, sintering 165°) were combined and purified by crystallisation (twice) from water, in which trans-*homocaronic acid* was much less soluble than *cis*-. It crystallised in needles, m. p. 190—191° (Found: C, 55·5; H, 7·0%; *M*, 172·4). In sodium carbonate solution the *trans*-acid was more stable to potassium permanganate than the *cis*-acid. It was readily converted into the anhydride of the latter by treatment with acetic anhydride, as described above.

From the sparingly soluble potassium salt (*A*), *cyclo*butane-1 : 2 : 3 : 4-tetracarboxylic acid, decomp. 285°, was obtained, which was identified by conversion into the methyl ester, m. p. 103°.

Action of Hydrogen Chloride on cis-*Homocaronic Acid.*—The acid (1·5 g.) was mixed with concentrated hydrochloric acid (10 c.c.), and heated in a sealed tube at 100° for 5 hours. After removal of the mineral acid on the water-bath, an oil remained which slowly solidified over sulphuric acid and potassium hydroxide in a vacuum. After draining on porous porcelain, the *lactone* crystallised from water in prisms, m. p. 91—92°, and further crystallisation from chloroform–ligroin gave six-sided plates, m. p. 101—102° [Found: C, 55·6; H, 6·7; *M*, 172·2, 170·2 (hot). $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%; *M*, 172]. The aqueous mother-liquor from which the lactone had separated was digested with barium hydroxide solution, filtered after removal of excess barium with carbon dioxide, and evaporated, but no sparingly soluble salt of terpenylic acid was obtained. The lactone was not attacked by hydriodic acid (*d* 1·7) and red phosphorus at 150°, whilst with hydriodic acid (*d* 1·9) complete degradation took place. It was neither reduced by sodium amalgam at 20° or 100°, nor oxidised by nitric acid (*d* 1·22).

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