CXXXIV.—*Studies in the Fenchene Series. Part I. A Synthesis of* apo*Fenchocamphoric Acid.*

By Wallace Frank Short.

Apart from the syntheses of *l*-β- and *d*-α-fenchene from nopinolacetic acid by Wallach (*Annalen*, 1907, **357**, 82; 1908, **363**, 1) and of *r*-fenchone by Ruzicka (*Ber.*, 1917, **50**, 1362), a *complete* synthesis has not yet been effected in the fenchene series. In order to achieve this, a favourable starting-point would appear to be *apo*fenchocamphoric acid. Hitherto this acid has been obtained from camphenilane by oxidation with nitric acid (Nametkin and Chuchrikovaia, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 425; Nametkin and Michailovna, *ibid.*, 1917, **49**, 417) and, in almost theoretical yield, from β-fenchocamphorone by oxidation with potassium permanganate (Komppa and Roschiev, *Ann. Acad. Sci. Fennicae*, 1917, *A*, **15**, 1; Roschiev, *ibid.*, 1919, *A*, **10**, 1; Komppa and Roschiev, *Annalen*, 1922, **429**, 175; Nametkin, *ibid.*, 1924, **438**, 185). It is regarded as 4 : 4-dimethyl*cyclo*pentane-1 : 3-dicarboxylic acid; this structure, however, has not been definitely established (compare Roberts, *J. Amer. Chem. Soc.*, 1926, **48**, 1975). The acid has now been synthesised by the condensation of *iso*butylene dibromide with ethyl disodiopropane-ααγγ-tetracarboxylate according to the classical methods of the Perkin school. The yield is very small owing to loss of bromine from the *iso*butylene dibromide with formation of *iso*butylene, α-bromo*iso*butylene, and other compounds, and is, moreover, adversely affected by slight variations in the conditions of preparation. Loss of hydrogen bromide was anticipated from the observations of other investigators (Bentley, J., 1895, **67**, 266), but the loss of both bromine atoms was somewhat unexpected, since Otto and Mühle (*J. pr. Chem.*, 1895, **51**, 519) state that *iso*butylene dibromide is attacked by sodium only with difficulty.

Although the synthesis is uneconomical, it establishes the constitution of *apo*fenchocamphoric acid as 4 : 4-dimethyl*cyclo*pentane-1 : 3-dicarboxylic acid.

EXPERIMENTAL.

Ethyl propane-ααγγ-tetracarboxylate (b. p. 194—195°/11 mm.) (88·5 g.; 1 mol.) and 130 c.c. of toluene were shaken with 9·2 g. (1½ atoms) of powdered sodium until this dissolved; 43·2 g. (¾ mol.) of *iso*butylene dibromide (b.p. 36—37°/10 mm.; Taboury, *Bull. Soc. chim.*, 1911, **9**, 125) were then added and the mixture was boiled for 60 hours. *iso*Butylene was steadily evolved and sodium bromide deposited. The product was poured into water and the oil so obtained was distilled under 10 mm. pressure. After removal of the substances boiling below 194°, there remained a small quantity of a thick syrup. This was boiled for 3 hours with 3 g. of potassium hydroxide dissolved in alcohol. The acid obtained on acidification, m. p. 170—179° (decomp.), was heated at 220—230° until the evolution of carbon dioxide had ceased. The semi-solid residue was washed twice with 10 c.c. of water, which extracted a small quantity of glutaric acid. The dried residue, m. p. 110—115°, was treated with 6 g. of acetyl chloride for 2 days, the excess of the latter then removed at 60° under reduced pressure, and the residue was shaken with 11 c.c. of cold 5% caustic soda solution, washed with water, dried, and recrystallised from benzene–light petroleum. It melted at 136—137°, and by solution in hot 10% caustic soda solution and reprecipitation with sulphuric acid, 0·6 g. of an acid (m. p. 143—145°) was obtained (*cis-apo*fenchocamphoric acid melts at 144·5—145°). From the acidified 5% caustic soda extract, crystals (1·3 g.) were deposited which melted at 147—148° after recrystallisation from ether (Found : C, 58·2 ; H, 7·6 by the micro-Pregl method ; equiv., 93·6. Calc. for $C_9H_{14}O_4$: C, 58·1 ; H, 7·5% ; equiv., 93·0). *trans-apo*Fenchocamphoric acid melts at 147—148° (Nametkin, *Annalen*, 1924, **438**, 185). The total yield of *apo*fenchocamphoric acid was 1·9 g. or 5% of the theoretical.

The author is indebted to the Chemical Society for a grant which partly defrayed the cost of this research, and to Prof. J. K. H. Inglis for an arrangement which prevented overlapping.

UNIVERSITY COLLEGE, AUCKLAND,
NEW ZEALAND.

[*Received, December 7th*, 1926.]