CCCCX.—*Preparation of* cis-o-*Carboxy*cyclo*hexaneacetic Acid.*

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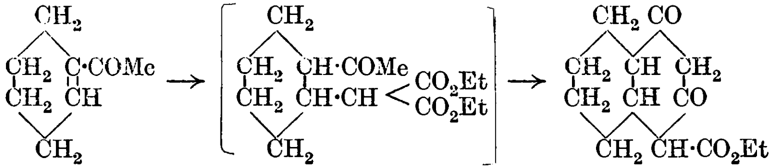
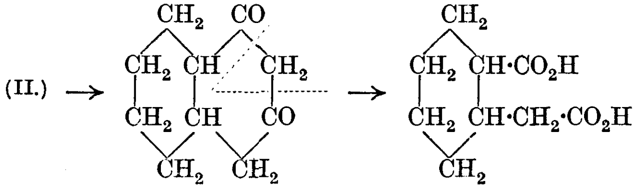
cis-o-CARBOXY*cyclo*HEXANEACETIC acid was first obtained by Windaus, Hückel, and Reverey (*Ber.*, 1923, **56**, 91), by a somewhat laborious method, as a mixture of *cis*- and *trans*-forms not easy to separate. This difficulty was partly overcome by Dutt (unpublished work), who obtained the pure *trans*-form by condensing ethyl Δ^1-*cyclo*hexenecarboxylate with ethyl cyanoacetate and hydrolysing the product. A method for the preparation of the pure *cis*-form has now been devised.

*cyclo*Hexenyl methyl ketone (I) readily condenses with ethyl sodiomalonate (compare Kon, this vol., p. 1792), giving *ethyl* 1 : 3-*diketodecahydronaphthalene*-4-*carboxylate* (II). This ester, on alkaline hydrolysis, passes into the diketone (III), which is in every way analogous to dimethyldihydroresorcinol and other well-known compounds of the same series. It is readily oxidised by alkaline hypobromite with formation of *cis-o*-carboxy*cyclo*hexaneacetic


(I.) (II.)

acid (IV), whereas the action of permanganate gives *trans-cyclo*hexane-1 : 2-dicarboxylic acid.



(II.) (III.) (IV.)

The yields are good throughout, although some difficulty is experienced in the preparation of *cyclo*hexenyl methyl ketone by Darzens's method (*Compt. rend.*, 1910, **150**, 707).

EXPERIMENTAL.

*cyclo*Hexenyl methyl ketone was prepared by the action of acetyl chloride on *cyclo*hexene in the presence of tin tetrachloride (Darzens, *loc. cit.*); the yield of ketone did not exceed 40% owing to the formation of resinous by-products.

The ketone (49 c.c.) was added to ethyl sodiomalonate, prepared from 64 c.c. of the ester and 10 g. of sodium in 140 c.c. of alcohol, and the mixture was heated on the steam-bath for 4 hours and kept over-night. Water was then added, neutral impurities removed with ether, the solution strongly acidified, and the precipitated oil taken up in ether. On removing the solvent, an oil was obtained which gradually solidified and crystallised well from ether–petroleum in needles, m. p. 114°, consisting of the *ester* (II). The yield was 80 g. or 60% (Found: C, 65·5; H, 7·6. $C_{13}H_{18}O_4$ requires C, 65·5; H, 7·6%). The compound is readily soluble in the usual organic solvents except petroleum and has the usual properties of compounds of this class; with ferric chloride it gives a brown colour which becomes redder and more intense on standing.

The keto-ester was hydrolysed with boiling aqueous barium hydroxide, but the product was liquid, probably owing to partial ring fission. With alcoholic potassium hydroxide the hydrolysis proceeded smoothly. The ester (24 g.) was heated over-night with 170 c.c. of 20% alcoholic alkali and the solution was diluted, extracted with ether, and acidified. On extraction with ether, an oil was obtained which gradually solidified; it was boiled with water, to which a little mineral acid had been added, to complete the removal of carbon dioxide. The *diketone* (III) crystallised as a yellow solid on cooling and formed needles, m. p. 142°, from dilute alcohol (yield, 60%) (Found: C, 71·9; H, 8·3. $C_{10}H_{14}O_2$ requires C, 72·2; H, 8·4%). With ferric chloride, it gives a brown coloration.

The diketone (III) (4 g.), dissolved in 10 c.c. of ice-cold 10% sodium hydroxide solution, was gradually added with shaking to an ice-cold hypobromite solution prepared from 6 g. of bromine neutralised with 10% aqueous sodium hydroxide (200 c.c.) and kept for ¾ hour. The precipitated bromoform was extracted with ether, the excess of bromine destroyed with sulphur dioxide, and the solution acidified with sulphuric acid and extracted with ether. The crude acid obtained, after several crystallisations from water, melted at 146—147° and was shown to consist of pure *cis-o*-carboxy*cyclo*hexaneacetic acid by the ready formation of the anhydride, m. p. 57°, on treatment with acetyl chloride (Found: C, 58·0; H, 7·4. Calc.: C, 58·1; H, 7·5%. Found in the disilver salt: Ag, 53·9. Calc.: Ag, 53·9%).

No *trans*-acid was isolated from the mother-liquors from the crystallisation of the *cis*-acid, although small quantities may have been present.

The diketone (4 g.), dissolved in 10 c.c. of 10% aqueous sodium hydroxide, was added to 260 c.c. of 5% potassium permanganate solution. After 48 hours, the excess of this reagent was destroyed with sulphur dioxide and the solution was acidified with sulphuric acid and extracted with ether. The extract on evaporation gave *trans-cyclo*hexane-1 : 2-dicarboxylic acid, m. p. 222° after recrystallisation from water (Found: C, 55·6; H, 7·0. Calc.: C, 55·8; H, 7·0%. Found in the disilver salt: Ag, 55·6. Calc.: Ag, 55·8%).

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