245. *Studies in the* cyclo*Hexane Series. Part III.* 1-*Carboxy*-3 : 3-*dimethyl*cyclo*hexane*-1-*acetic Acid.*

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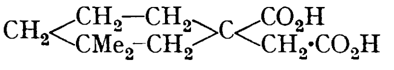
The synthesis of 1-*carboxy*-3 : 3-*dimethyl*cyclo*hexane*-1-*acetic acid*, in which the damping effect of the *gem*-dimethyl group might be expected to facilitate the isolation of strainless isomers, was undertaken in continuation of the study of the isomeric 1-carboxymethyl*cyclo*hexane-1-acetic acids (Desai, Hunter, Ghulam Khan, and Saharia, this vol., p. 416). Condensation of *ethyl* 3 : 3-*dimethyl*-cyclo*hexylidene*-1-*cyanoacetate*, obtained from Crossley and Renouf's ketone (J., 1907, **91**, 63), with potassium cyanide, and subsequent hydrolysis of the product gave the required acid, accompanied by a small amount of an *amic acid*. It was also prepared by hydrolysis of *ethyl* 1-*cyano*-3 : 3-*dimethyl*cyclo*hexane*-1-α-*cyanoacetate* obtained by Higson and Thorpe's method (J., 1906, **89**, 1455). As might be anticipated from thermodynamical considerations based on the energy associated with angular strain in homocyclic rings, which indicate that the *cyclo*hexane ring should be able to change from the " C " to the " Z " form at almost every collision, we were unable to obtain any evidence for the existence of a second form of 1-carboxy-3 : 3-dimethyl*cyclo*hexane-1-acetic acid.



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2-CH_2}\\ \mathrm{CMe_2-CH_2}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CO_2H}\\ \mathrm{CH_2\cdot CO_2H}\end{matrix}$$

Experimental.

1-*Carboxy*-3 : 3-*dimethyl*cyclo*hexane*-1-*acetic Acid*.—(a) *Lapworth and McRae's method*. A mixture of 3 : 3-dimethyl*cyclo*hexanone (25 g.) and ethyl cyanoacetate (23 g.) to which piperidine (10—15 drops) had been added was kept over-night, and heated on a water-bath for 48 hours after addition of anhydrous sodium sulphate (10 g.). The mixture was extracted with ether, the extract washed with dilute hydrochloric acid, dried, and distilled; unchanged material was obtained (which was subsequently worked up again), followed by the *cyano-ester*, b. p. 155—157°/14 mm. (Found : C, 70·3; H, 8·8. $C_{13}H_{19}O_2N$ requires C, 70·6; H, 8·6%); yield 50—55%. A solution of potassium cyanide (8 g.) in water (25 c.c.) was gradually added to the cyano-ester (14 g.) in rectified spirit (75 c.c.); heat was evolved, and the mixture was kept at laboratory temperature for 24 hours. The product obtained by removal of alcohol was treated with water and with concentrated hydrochloric acid (100 c.c.), and the mixture heated on a sand bath, under reflux, for 48 hours; the solid which separated on cooling was collected, and the mother-liquors were extracted with ether. The combined solution of the solid product in ether and the ethereal extract was exhaustively extracted with aqueous sodium carbonate, and this extract was acidified. The product isolated by extraction with ether was rubbed with benzene to remove sticky impurities and thereafter recrystallised from dilute alcohol, 1-*carboxy*-3 : 3-*dimethyl*-cyclo*hexane*-1-*acetic acid* being obtained in needles, m. p. 166° (efferv.) [Found : C, 61·5; H, 8·5; equiv., 108. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·4%; equiv. (dibasic), 107]. The barium, lead, and copper salts of this acid were precipitated on the addition of aqueous salts of the metals to a neutral solution of the ammonium salt. The calcium salt, similarly prepared, separated on warming. The *anhydride* was obtained by heating the acid in a hard-glass tube at 170—180° for an hour, and solidified on cooling. On recrystallisation from benzene it was obtained in prismatic needles, m. p. 67° (Found : C, 67·6; H, 8·3. $C_{11}H_{16}O_3$ requires C, 67·4; H, 8·2%). The *anilic acid* separated on mixing benzene solutions of the anhydride and aniline, and crystallised from dilute alcohol in plates, m. p. 205° (Found : C, 70·6; H, 7·8. $C_{17}H_{23}O_3N$ requires C, 70·6; H, 7·9%). The *anil*, obtained by heating the anilic acid at 180° for 3 hours, solidified on being rubbed with aqueous ammonia. On recrystallisation from dilute alcohol, it formed small lustrous plates, m. p. 132° (Found : C, 75·1; H, 7·8. $C_{17}H_{21}O_2N$ requires C, 75·3; H, 7·8%).

The benzene extract of gummy material which contaminated the crude dimethyl*cyclo*hexane acid was evaporated in a vacuum, and the gum obtained solidified on keeping, m. p. 170—185°. On recrystallisation from dilute alcohol, this gave a more sparingly soluble fraction consisting of the *imide* of 1-carboxy-3 : 3-dimethyl*cyclo*hexane-1-acetic acid, which was also prepared by heating the dry ammonium salt of the acid at 180°, and formed lustrous plates, m. p. 204° (Found : C, 67·9; H, 8·6. $C_{11}H_{17}O_2N$ requires C, 67·8; H, 8·7%). The more soluble fraction consisted of an *amic acid*, which crystallised from benzene in soft needles, m. p. 145° (Found :

C, 61·9; H, 8·9. $C_{11}H_{19}O_3N$ requires C, 62·0; H, 8·9%). This gave the acid of m. p. 166° on hydrolysis with mineral acids and alkali. The neutral product recovered from the original ethereal extract of the hydrolysis of the dicyano-ester gave a nitrogenous substance which crystallised from hexane in prismatic needles, m. p. 85—86°, and also gave the acid, m. p. 166°, on hydrolysis with acid and alkali. This was probably the dinitrile corresponding to the dimethyl*cyclo*hexane acid, but the quantity at our disposal was insufficient for detailed investigation.

(b) *Higson and Thorpe's method.* Potassium cyanide (8 g.) in water (25 c.c.) was gradually added to the clear solution obtained from 3 : 3-dimethyl*cyclo*hexanone (12·6 g.) and sodium bisulphite (11 g.) in water (50 c.c.) previously treated with sulphur dioxide. The oil was extracted in ether, washed with saturated brine, dried, and distilled under reduced pressure, 1-*hydroxy*-1-*cyano*-3 : 3-*dimethyl*cyclo*hexane* being obtained, b. p. 128—129°/15 mm. (Found : C, 70·3; H, 9·9. $C_9H_{15}ON$ requires C, 70·6; H, 9·8%); yield 75—80%. A suspension of ethyl sodiocyanoacetate (sodium, 1·1 g.; alcohol, 15 c.c.; ethyl cyanoacetate, 6 g.) was added with shaking to the cyanohydrin (7·5 g.) in absolute alcohol (10 c.c.) and the mixture was kept for 24 hours and thereafter heated on a water-bath for 2 hours. The oil obtained on dilution with water and acidification was extracted and dried in ether and distilled, the dicyano-ester passing over at 180—195°/15 mm. On redistillation, *ethyl* 1-*cyano*-3 : 3-*dimethyl*cyclo*hexane*-1-α-*cyanoacetate* was obtained as a pale yellow liquid, b. p. 190—191°/15 mm. (Found : C, 67·9; H, 8·2. $C_{14}H_{20}O_2N_2$ requires C, 67·7; H, 8·0%). The ester was hydrolysed by heating with concentrated hydrochloric acid for 48 hours, 1-carboxy-3 : 3-dimethyl*cyclo*hexane-1-acetic acid, m. p. 166°, being obtained.

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