## 43. *Reactions of Methyl $\Delta^{\beta}$-Propene-$\alpha\alpha\beta$-tricarboxylate. An Example of Three-carbon Ring-chain Prototropy involving a Simple* cyclo*Propane Ring.*

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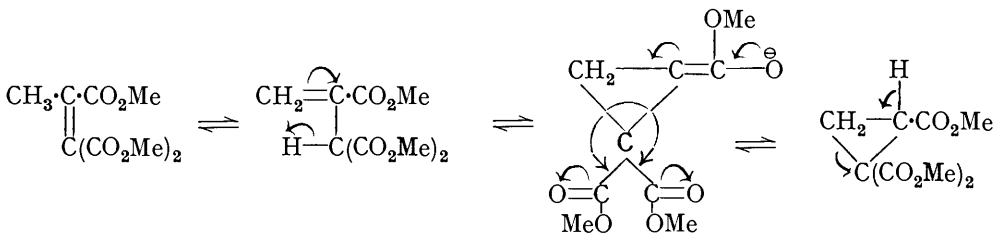
ALTHOUGH an unequivocal example of three-carbon ring-chain prototropy involving the formation of a *cyclo*butane ring is provided by the self-condensation of various glutaconic esters (Ingold, Perren, and Thorpe, J., 1922, **121**, 1765), no conclusive evidence has hitherto been obtained for the simplest case involving the reversible formation of a *cyclo*propane ring (cf. Baker, J., 1925, **127**, 985, 1682). Evidence has now been obtained of the reversible interconversion of the open-chain propene ester (II) and its cyclic tautomeride (IV), in which the *cyclo*propane ring is presumably stabilised by the spatial effect of the carbomethoxy-groups, which will also greatly increase the ionisability of the mobile hydrogen and confer high mobility on the electromeric system involved. Interconversion presumably occurs through the mesomeric ion (III), which must possess a high degree of degeneracy.



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

It has already been noted (J., 1934, 1467) that methyl $\Delta^{\beta}$-propene-$\alpha\alpha\beta$-tricarboxylate (II) is the main product of the action of warm pyridine on methyl $\alpha$-bromo-*n*-propane-

$\alpha\alpha\beta$-tricarboxylate (V, R = Br), the $\Delta^{\alpha}$-ester (I), which is presumably the initial product, undergoing prototropic change into the $\Delta^{\beta}$-ester, which, on the basis of the known effect of a β-carbomethoxy-substituent (Shoppee, J., 1930, 968), would be expected to be the more stable open-chain form.

$\begin{matrix}\mathrm{CHMe{\cdot}CO_2Me}\\ \mathrm{CR(CO_2Me)_2}\end{matrix}$ (V.) $\qquad$ $\begin{matrix}\mathrm{CH_2Br{\cdot}CH{\cdot}CO_2Me}\\ \mathrm{CH(CO_2Me)_2}\end{matrix}$ (VI.) $\qquad$ $\begin{matrix}\mathrm{CMeBr{\cdot}CO_2Me}\\ \mathrm{CH(CO_2Me)_2}\end{matrix}$ (VII.)

There can be little doubt as to the structure of the original α-bromo-ester (V, R = Br), since this is obtained by direct bromination of the malonyl hydrogen in the parent saturated ester (V, R = H) (Baker, J., 1933, 811). Moreover, reduction of the α-bromo-ester regenerates the original saturated parent. The presence of a methylene group in the $\Delta^{\beta}$-ester (II) is proved by the production of formaldehyde upon ozonolysis, further confirmation of its constitution being provided by the structure of the product obtained by addition of hydrogen bromide. The solid bromo-ester, m. p. 70°, so obtained is methyl γ-bromo-*n*-propane-$\alpha\alpha\beta$-tricarboxylate (VI) (J., 1934, 1467), since it condenses with methyl sodiomalonate to give, not methyl β-methyl-*n*-propane-$\alpha\alpha\beta\gamma\gamma$-pentacarboxylate as previously supposed (J., 1933, 811), but *methyl* n-*butane-*$\alpha\alpha\beta\delta\delta$*-pentacarboxylate* (VIII), which is hydrolysed by boiling concentrated hydrochloric acid to *n*-butane-$\alpha\beta\delta$-tricarboxylic acid identical with a specimen obtained by similar hydrolysis of ethyl *n*-butane-$\alpha\beta\beta\delta$-tetracarboxylate (Kay and Perkin, J., 1906, **89**, 1642).

$\begin{matrix}\mathrm{CH(CO_2Me)_2}\\ \mathrm{CH_2}\\ \mathrm{CH{\cdot}CO_2Me}\\ \mathrm{CH(CO_2Me)_2}\end{matrix}$ (VIII.) $\qquad$ $\begin{matrix}\mathrm{CH(CO_2Me)_2}\\ \mathrm{CH_2}\\ \mathrm{CH{\cdot}CO_2Me}\\ \mathrm{C(CO_2Me)_2}\\ \mathrm{CH_2{\cdot}CO_2Me}\end{matrix}$ (IX.) $\qquad$ $\begin{matrix}\mathrm{CH_2{\cdot}CO_2Me}\\ \mathrm{C(CO_2Me)_2}\\ \mathrm{CH_2}\\ \mathrm{CH{\cdot}CO_2Me}\\ \mathrm{CH(CO_2Me)_2}\end{matrix}$ (X.)

The formation of the γ-bromo-ester (VI) can be satisfactorily explained only if the unsaturated ester has the structure (II).

Evidence of the prototropic interconversion of the $\Delta^{\alpha}$- and the $\Delta^{\beta}$-ester was forthcoming by re-examination of the products obtained by the addition of hydrogen bromide to the unsaturated ester. When contact with the hydrogen bromide (in acetic acid) was prolonged (10 days), or when the unsaturated ester, recovered as a by-product in the preparation of (VIII) by condensation of the γ-bromo-ester (VI) with methyl sodiomalonate, was employed, the resultant crude solid bromo-ester had a much lower m. p. (45°) than that usually observed, and fractional crystallisation from ligroin separated it into the less soluble γ-bromo-ester (VI), m. p. 70°, and a small amount of a very soluble, isomeric bromo-ester, m. p. 54°, which must be *methyl* β-*bromo*-n-*propane-*$\alpha\alpha\beta$*-tricarboxylate* (VII). The two bromo-esters cannot be dimorphous forms, since they could not be interconverted and, moreover, in one crystallisation the two very distinctive types of crystal (clusters of fine needles, m. p. 64—65°, and large stout prisms, m. p. 52—54°, respectively) were obtained side by side; they were mechanically separated, and depressed each other's melting point to 45°. There is, of course, the possibility that the β-bromo-ester (VII) is derived from the $\Delta^{\beta}$-ester (II) by a reverse hydrogen bromide addition, but this explanation is rendered highly improbable by the fact that, when the pure $\Delta^{\beta}$-ester (below) was employed, *only* the γ-bromo-ester could be isolated. The β-bromo-ester is therefore almost certainly obtained by normal addition of hydrogen bromide to the $\Delta^{\alpha}$-ester (I) present in the equilibrium mixture of $\Delta^{\alpha}$- and $\Delta^{\beta}$-esters resulting from the catalytic action of pyridine or sodium methoxide respectively. The direct action of methyl-alcoholic sodium methoxide on the $\Delta^{\beta}$-ester is referred to later. The isolated observation (J., 1933, 814) that mesaconic acid was obtained by hydrolysis of the parent unsaturated ester with methyl-alcoholic potassium hydroxide is readily understood in the light of the results of Linstead and Mann (J., 1931, 726) concerning the position of equilibrium attained in the propene-$\alpha\beta$-dicarboxylic acids

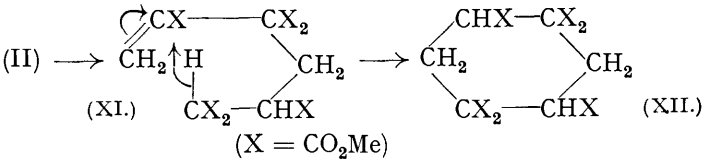
(70% mesaconic acid) in the presence of hot alkali. Hydrolysis with boiling concentrated hydrochloric acid affords itaconic acid.

In order to obtain a pure specimen of the Δ$^{\beta}$-ester, the original unsaturated ester was converted into its sodium derivative in dry ether, and this was decomposed by a slight deficiency of benzoic acid (Kon and Watson, J., 1932, 1). The resulting Δ$^{\beta}$-ester, b. p. 139°/1·9 mm., exhibits no essential change in properties. It gives formaldehyde on ozonolysis, but with hydrogen bromide affords *only* the γ-bromo-ester.

Evidence of its tautomeric interconversion into the *cyclo*propane ester (IV) is provided by the formation of *cyclo*propane-1 : 1 : 2-tricarboxylic acid when the Δ$^{\beta}$-ester is hydrolysed with concentrated methyl-alcoholic potassium hydroxide. Incidentally the same acid is also obtained (possibly by direct elimination of hydrogen bromide) when the γ-bromo-ester is similarly hydrolysed, a reaction which further confirms the structure assigned to the latter ester. There is, of course, a possible alternative explanation to ring-chain prototropic change for the production of the *cyclo*propane acid from the Δ$^{\beta}$-propene ester, *viz.*, the intermediate formation of the γ-methoxy-ester, which then undergoes ring-closure with fission of methyl alcohol. Unfortunately, such an explanation cannot be definitely excluded, since attempts to prepare the methoxy-ester, by the action either of silver acetate and methyl alcohol, or of dry sodium methoxide (1 mol.) in dry ether, on the γ-bromo-ester (VI) resulted in the formation of methyl *cyclo*propane-1 : 1 : 2-tricarboxylate.

When, however, ethyl *cyclo*propane-1 : 1 : 2-tricarboxylate (Conrad and Guthzeit, *Ber.*, 1884, **17**, 1186), which, as expected, is saturated to potassium permanganate and gives no formaldehyde upon ozonolysis, is submitted to short treatment with boiling methyl-alcoholic sodium methoxide, the recovered ester contains unsaturated material and, on ozonolysis, formaldehyde is readily isolated as its dimedon compound. The most feasible explanation of this observation is a ring-chain prototropic change catalysed by alkoxide ion, the only alternative explanation being the rather distasteful hypothesis of addition and subsequent fission of methyl alcohol (in a different direction) during the one experimental process.

When the Δ$^{\beta}$-unsaturated ester (II) is treated with *N*-methyl-alcoholic sodium methoxide (1 mol.), the main initial reaction is a Michael condensation affording the unsaturated dimeric ester (XI), which then undergoes a further internal Michael reaction to give saturated *methyl* cyclo*hexane*-1 : 1 : 2 : 4 : 4 : 5-*hexacarboxylate* (XII) : this is isolated as one of the main products of the reaction. Hydrolysis affords cyclo*hexane*-1 : 2 : 4 : 5-*tetracarboxylic acid*, dehydrogenated by selenium to pyromellitic acid.




The actual isolation of the unsaturated ester (XI) has not been achieved. Treatment of the unsaturated gum [from which the crystalline ester (XII) had separated] with hydrogen bromide in acetic acid afforded the bromo-ester (VI) [from unchanged (II)] and a (?) *stereoisomeride* of the saturated ester (XII).

Thus, under the influence of alkali the Δ$^{\beta}$-propene ester (II) may undergo either a reversible intramolecular Michael change to give the *cyclo*propane ester (IV) (ring-chain tautomerism), or an intermolecular condensation to afford the dimeric ester (XI), in which a further internal Michael condensation then takes place. A quantitative examination of the triple tautomeric system, (I) ⇌ (II) ⇌ (IV), would therefore probably be complicated and has not yet been attempted, but the results obtained suggest that the proportion of (I) present at equilibrium is very small, and that the equilibrium is located mainly in the direction of (IV).

The structure (VIII) which it is now necessary to assign to the condensation product of the γ-bromo-ester and methyl sodiomalonate means that the synthesis of esters of the type $CHX_2 \cdot CMeX \cdot CHX_2$ (*loc. cit.*) still remains unachieved, and the ester (VIII) is, of course,

valueless as an intermediate in the synthesis of the bile acid degradation product $C_{13}H_{20}O_6$. Before the true constitution of (VIII) had been established, however, several successive steps in the synthesis had been carried out. Condensation of the sodium derivative of (VIII) with methyl iodoacetate affords (probably) *methyl* n-*pentane*-$\alpha\beta\beta\gamma\varepsilon\varepsilon$-*hexacarboxylate* (IX), although the alternative structure (X), involving condensation with the other malonic residue of (VIII), cannot be excluded. Hydrolysis of (IX) affords a n-*pentane-tetracarboxylic acid* ($\alpha\beta\gamma\varepsilon$- or $\alpha\beta\delta\varepsilon$-), the *methyl* ester of which undergoes a Dieckmann reaction to give a *methyl* cyclo*hexanonetricarboxylate* (2 : 3 : 4-, 2 : 4 : 5-, or 2 : 3 : 5-).

## Experimental.*

*Methyl $\Delta^{\beta}$-Propene-$\alpha\alpha\beta$-tricarboxylate* (II) (813).—This ester and not the $\Delta^{\alpha}$-ester appears to be the main product of the action of pyridine on methyl $\alpha$-bromo-*n*-propane-$\alpha\alpha\beta$-tricarboxylate. The bromo-ester (50 g.) was added to 30 g. of pyridine; the mixture was gently warmed on the steam-bath for ½ hour, left at room temperature for 24 hours, and again warmed for ½ hour. After cooling, it was largely diluted with dry ether, the precipitated pyridine hydrobromide filtered off and washed with dry ether, and the combined filtrates, after removal of ether, fractionally distilled under reduced pressure. After distillation of the excess of pyridine, the unsaturated ester (25 g.) distilled at 150°/15 mm. A few grams of unchanged bromo-ester were recovered, b. p. *ca.* 160°/7 mm. This procedure eliminates the successive treatment with pyridine previously found to be necessary. To obtain the pure $\Delta^{\beta}$-ester, 1·5 g. of sodium dissolved in 10—15 c.c. of dry methyl alcohol were evaporated to dryness in a vacuum, the residual sodium methoxide was evaporated three times with dry ether, and 10·8 g. of the " recovered " unsaturated ester in 50 c.c. of ether were added. Addition of 75 c.c. of ligroin (b. p. 60—80°) precipitated the slightly sticky sodium derivative, which was shaken with 6 g. of benzoic acid (theory, 6·1 g.) for 18 hours. The liquid was filtered, the solvent evaporated, and the residue distilled. After about 3 g. had been collected at 130—135°/2·5 mm., 5·5 g. of the $\Delta^{\beta}$-*ester* distilled at 132°/1·9 mm.

*Ozonolysis.* Essentially similar results were obtained by ozonolysis of all specimens of the unsaturated ester in hexane solution for 48 hours. After evaporation of the solvent at room temperature in a vacuum, the ozonide was decomposed with cold water, with addition of dilute sodium hydrogen carbonate solution to neutralise the acid formed. The neutral product was extracted with ether and obtained as a colourless syrup. Since in no case did the product give a colour with ferric chloride, this neutral product is probably a mixture of further degradation products of the primary product, methyl oxalylmalonate, but none of these could be definitely identified. With semicarbazide acetate, only minute yields of semicarbazones, too small for identification, were obtained. Distillation of the aqueous sodium hydrogen carbonate solution gave formaldehyde, isolated as its dimedon compound, m. p. and mixed m. p. 189—190°. From the undistilled aqueous liquor, after evaporation to dryness and acidification with cold concentrated hydrochloric acid, was isolated a brown syrup, from which some oxalic acid dihydrate, m. p. 99°, raised to 102° by admixture with a genuine specimen, was obtained, and was identified by the usual tests. Distillation of the liquid portion gave a little formic acid, b. p. 100°, and a fraction, b. p. 160—170°/17 mm., which could not be identified.

*Hydrolysis of the $\Delta^{\beta}$-ester.* (a) With concentrated hydrochloric acid. After hydrolysis for 2 hours, evaporation of the acid liquid on a steam-bath gave itaconic acid, m. p. and mixed m. p. 165° (Found : equiv. by microtitration, 67·7. Calc. for $C_5H_6O_4$ : equiv., 65).

(b) With methyl-alcoholic potassium hydroxide. Heated for a short time on a steam-bath with a moderately concentrated solution of potassium hydroxide in dry methyl alcohol, the $\Delta^{\beta}$-ester afforded a solid potassium salt. This was separated, washed with ether, and decomposed with cold, moderately concentrated hydrochloric acid; ether then extracted *cyclo*propane-1 : 1 : 2-tricarboxylic acid, m. p. [after crystallisation from ether–ligroin (b. p. 40—60°)] and mixed m. p. 187° (Found : C, 41·1; H, 3·7; equiv., by microtitration, 62·3. Calc. for $C_6H_6O_6$ : C, 41·4; H, 3·45%; equiv., 58).

*Addition of Hydrogen Bromide to the Unsaturated Ester.*—The original unsaturated ester (65 g.) was added to 70 c.c. of 55% (wt./vol.) hydrogen bromide in acetic acid. After being kept for 3 days at room temperature, the solution was poured into ice-water and extracted with ether; the extract was washed (water, sodium carbonate solution, water), dried (calcium

* Compounds previously assigned erroneous structures are now correctly described, and are identified by the addition, in parentheses, of the page reference (J., 1932) to their original description.

chloride), and evaporated. The residue crystallised when seeded, giving 58 g. of approximately pure methyl γ-bromo-*n*-propane-ααβ-tricarboxylate (814), m. p. 60—65°. Crystallisation from ether–ligroin raised the m. p. to 70°. With boiling methyl-alcoholic potassium iodide the γ-bromo-ester afforded the corresponding γ-iodo-ester (814), m. p. 74°. Similar addition of hydrogen bromide to the unsaturated ester, b. p. 120—140°/1 mm., recovered in the preparation of the ester (VIII) (below) gave a crystalline product, m. p. 45°, unchanged by recrystallisation from ether–ligroin. Reduction of this mixture of bromo-esters with zinc dust and boiling methyl alcohol containing 1 drop of dilute acetic acid gave methyl *n*-propane-ααβ-tricarboxylate, m. p. and mixed m. p. 48°. When a moderately dilute solution of the mixed bromo-esters, m. p. 45°, in ether–ligroin was seeded with the γ-bromo-ester, m. p. 70°, this compound alone crystallised in clusters of needles. The mother-liquor slowly deposited a small quantity of large well-formed prisms of *methyl* β-*bromo*-n-*propane*-ααβ-*tricarboxylate*, m. p. 55° after recrystallisation from ligroin (b. p. 40—60°) (Found: C, 36·3; H, 4·55; Br, 27·2. $C_9H_{13}O_6Br$ requires C, 36·4; H, 4·4; Br, 26·9%). The m. p. is depressed to 45° by admixture with the γ-bromo-ester. In one crystallisation clusters of needles, m. p. 64—65°, and prisms, m. p. 52—54°, depressed to 45° by admixture, were obtained side by side, and could be separated by hand. When an ether–ligroin solution of the γ-bromo-ester, m. p. 70°, was seeded with the β-bromo-ester, m. p. 55°, only the γ-bromo-ester, m. p. 70°, crystallised. Boiled for 24 hours with alcoholic potassium iodide, the β-bromo-ester afforded a *liquid* iodo-ester which would not crystallise even after seeding with the γ-iodo-ester, m. p. 74°.

Hydrolysis of the γ-bromo-ester with methyl-alcoholic potassium hydroxide under the same conditions as those employed with the unsaturated ester afforded *cyclo*propane-1 : 1 : 2-tricarboxylic acid (m. p. and mixed m. p.).

*Conversion of Ethyl* cyclo*Propane*-1 : 1 : 2-*tricarboxylate into its Open-chain Isomeride.*—Ethyl *cyclo*propane-1 : 1 : 2-tricarboxylate, b. p. 133—134°/1·6 mm. (Conrad and Guthzeit, *loc. cit.*), is saturated to aqueous potassium permanganate–sodium hydrogen carbonate and, after ozonolysis for 2 hours in hexane solution, evaporation of the solvent in a vacuum, decomposition with cold water and distillation, gives no precipitate with an alcoholic solution of dimedon. The same ester (1 g.) was refluxed on a steam-bath with a solution of 0·1 g. of sodium in 3 c.c. of dry methyl alcohol for 1½ hours: the neutral fraction (unsaturated to permanganate), on similar ozonolysis, afforded formaldehyde (dimedon compound, m. p. and mixed m. p. 189—190°).

*Methyl* cyclo*Hexane*-1 : 1 : 2 : 4 : 4 : 5-*hexacarboxylate* (XII).—The $\Delta^{\beta}$-propene ester (10·8 g.) was added to a cold solution of 1·15 g. of sodium in 50 c.c. of dry methyl alcohol, and the mixture refluxed on a steam-bath for 1½ hours. The deep yellow solution was poured into brine, and the neutral fraction isolated in the usual manner. Concentration of the dry ethereal solution caused crystallisation (1·7 g.) of the *ester*, m. p. 181° after recrystallisation from absolute methyl alcohol (Found: C, 50·1; H, 5·5; *M*, in camphor, 398, 410. $C_{18}H_{24}O_{12}$ requires C, 50·0; H, 5·6%; *M*, 432). Distillation of a portion of the syrupy yellow mother-liquor (6·7 g.) afforded fractions, b. p. approx. 130°/3 mm. and 130—145°/3 mm., which were highly unsaturated and probably consisted mainly of the unchanged $\Delta^{\beta}$-propene ester. Subsequently much decomposition set in and a small fraction of a highly viscous, yellow syrup, b. p. 220°/3 mm., was obtained. This contained unsaturated material, but, when kept with a little ether deposited crystalline material, m. p. 154—164° after recrystallisation from methyl alcohol. The m. p. was raised to 154—175° by admixture with the hexacarboxylic ester, m. p. 181°, and it is possible that the material is a further quantity of this ester possibly contaminated with a stereoisomeric form. This material was not further investigated. The neutral product isolated after the prolonged action (4 days) of 55% (wt./vol.) hydrogen bromide in acetic acid on the unsaturated residue, partly crystallised. After draining on porous porcelain and crystallisation from ether–ligroin (b. p. 40—60°), a bromine-free product, probably a *stereoisomeride*, m. p. 125—126°, was obtained (Found: C, 49·9; H, 5·6%; *M*, 351, 343). The mother-liquor slowly deposited a small amount of the γ-bromo-ester, m. p. and mixed m. p. 67—70°.

Hydrolysis of the saturated ester with boiling concentrated hydrochloric acid for 3 hours and evaporation on a steam-bath afforded crystalline cyclo*hexane*-1 : 2 : 4 : 5-*tetracarboxylic acid*, which was difficult to purify. After recrystallisation from concentrated hydrochloric acid, draining on porous porcelain, and washing with cold ether, it had m. p. 217° (decomp.) (Found: C, 42·4; H, 4·6; equiv., by microtitration, 75. $C_{10}H_{12}O_8$ requires C, 46·2; H, 4·6%; equiv., 65). It was characterised as its *methyl* ester, m. p. 88°, obtained by long esterification with methyl-alcoholic hydrogen chloride containing one drop of concentrated sulphuric acid; the neutral product crystallised and was recrystallised from ether–ligroin (b. p. 40—60°) (Found:

C, 53·1; H, 6·2. $C_{14}H_{20}O_8$ requires C, 53·2; H, 6·3%). The ester is probably a mixture of stereoisomerides. Dehydrogenation of the acid (0·2 g.), m. p. 217°, was effected by heating with powdered selenium at 310° for 2 hours. The cooled mixture was extracted with hot sodium carbonate solution, and this solution extracted with ether, acidified with hydrochloric acid, and again extracted with ether. The acid residue from the dried ethereal solution was refluxed with methyl-alcoholic hydrogen chloride for 3—4 hours. The neutral fraction gave crystalline material, m. p. 127° after one recrystallisation from ether–ligroin (b. p. 40—60°); the quantity was insufficient for further purification, but mixed with genuine methyl pyromellitate (m. p. 141°), its m. p. was raised to 138—139°.

*Attempts to prepare the $\gamma$-Methoxy-ester.*—The corresponding $\gamma$-bromo-ester (2·1 g.) was shaken with 1·7 g. of silver acetate in 30 c.c. of dry methyl alcohol for 12 hours. Since no apparent action had occurred, the mixture was refluxed on a steam-bath for 4 hours, cooled, and diluted with dry ether, and the silver salts removed. Evaporation of the filtrate left a colourless syrup which would not crystallise, but by distillation afforded methyl *cyclo*propane-1 : 1 : 2-tricarboxylate, b. p. 109°/0·8 mm. (Found : C, 49·7; H, 5·6; OMe, 42·6. Calc. for $C_9H_{12}O_6$ : C, 50·0; H, 5·6; OMe, 43·0%). The same ester, b. p. 115°/1·0 mm., was obtained when 2 g. of the $\gamma$-bromo-ester were shaken with dry sodium methoxide (from 0·155 g. of sodium) in anhydrous ether, and the mixture left at room temperature for 18 hours. Saturated with dry ammonia in dry methyl alcohol, it afforded the *triamide*, m. p. 238° (decomp.) after crystallisation from aqueous methyl alcohol (Found : C, 43·1; H, 5·6; N, 24·6. $C_6H_9O_3N_3$ requires C, 42·1; H, 5·3; N, 24·6%).

Hydrolysis of this ester with the same solution of methyl-alcoholic potassium hydroxide as was employed in the hydrolysis of the unsaturated ester, and isolation of the acid product in the usual manner, gave a colourless syrup which immediately crystallised when rubbed. It was a *methyl dihydrogen* ester, m. p. 169°, and was purified by crystallisation from ether–ligroin (b. p. 40—60°) [Found : C, 44·8; H, 4·5; OMe, 17·9; equiv., by titration, 93·9. $C_7H_8O_6$ requires C, 44·7; H, 4·3; OMe, 16·5%; equiv. (dibasic), 94·0]. Hydrolysis with concentrated aqueous potassium hydroxide containing a little methyl alcohol gave *cyclo*propane-1 : 1 : 2-tricarboxylic acid, m. p. and mixed m. p. 187° (decomp.).

*Methyl* n-*Butane-$\alpha\alpha\beta\delta\delta$-pentacarboxylate* (VIII) (814).—To a solution of 4·15 g. of sodium in 50 c.c. of dry methyl alcohol were added 31 g. of methyl malonate; the mixture was refluxed for 10 minutes and cooled, and a warm solution of 53·5 g. of methyl $\gamma$-bromo-*n*-propane-$\alpha\alpha\beta$-tricarboxylate in dry methyl alcohol added. Separation of sodium bromide occurred with evolution of heat. The mixture was kept at room temperature for 18 hours and then refluxed on a steam-bath till neutral (2—3 hours). Distillation of the neutral fraction, isolated in the usual manner, gave a small amount of low fraction and then some recovered unsaturated ester, b. p. 120—140°/1 mm. The residue crystallised when seeded and afforded 20 g. of the butane ester, m. p. 88° * after crystallisation from ether–ligroin (b. p. 40—60°). Hydrolysis of this ester with boiling concentrated hydrochloric acid for 1 hour and complete evaporation on a steam-bath gave *n*-butanetricarboxylic acid, m. p. 120°, raised to 122° by admixture with a genuine specimen (Kay and Perkin, *loc. cit.*).

*Methyl* n-*Pentane-(?)$\alpha\beta\beta\gamma\varepsilon\varepsilon$-hexacarboxylate* (IX).—To a solution of 1·53 g. of sodium in 50 c.c. of dry methyl alcohol were added 23·2 g. of the butanepentacarboxylate, and the solution warmed on the steam-bath for a few minutes. To the cooled solution, 13·5 g. of methyl iodoacetate were added; the mixture was kept at room temperature for 1½ hours and then refluxed for 1½ hours on a steam-bath. Distillation of the neutral fraction, isolated in the usual manner, afforded 20 g. of the *hexacarboxylate*, b. p. *ca.* 240°/4 mm., as a colourless, exceedingly viscous syrup (Found : C, 48·7; H, 5·9. $C_{17}H_{24}O_{12}$ requires C, 48·6; H, 5·7%).

The ester (20 g.) was hydrolysed for 6 hours with 60 c.c. of boiling concentrated hydrochloric acid, and the liquor evaporated to dryness on a steam-bath. The viscous residue partly crystallised, and trituration with dry ether to remove gummy material left n-*pentane-(?)$\alpha\beta\gamma\varepsilon$-tetracarboxylic acid*, m. p. 204—205° after crystallisation from ether containing a little acetone (Found : C, 43·7; H, 5·0; equiv., by titration, 62·8. $C_9H_{12}O_8$ requires C, 43·5; H, 4·8%; equiv., 62·0). The acid is readily purified through its *barium* salt, the solubility of which is greater in cold than in hot water (Found : Ba, 46·5; $H_2O$, by heating an air-dried specimen at 140°, 11·1. $C_9H_8O_8Ba_2,4H_2O$ requires Ba, 46·5; $H_2O$, 12·2%). The last molecule of water is difficult to remove. The *methyl* ester, b. p. 180°/0·8 mm., was prepared by the action of methyl iodide on a paste of the dry silver salt and ether (Found : C, 50·9; H, 6·7. $C_{13}H_{20}O_8$ requires C, 51·3; H, 6·6%).

* The m. p. 58° previously given (*loc. cit.*) is a misprint.

*Methyl* cyclo*Hexanonetricarboxylate.*—The above tetramethyl ester (3 g.) in dry toluene was added to 0·23 g. of " molecular " sodium in the same medium, and the whole refluxed for 4—5 hours. The solution darkened, but much sodium remained undissolved. A drop or two of dry methyl alcohol was added and, after further refluxing to dissolve all the sodium, the cooled solution was decomposed with ice, and the alkaline solution extracted with ether. The aqueous alkaline liquor was dropped into ice-cold dilute hydrochloric acid, which was then extracted with ether. True acid products were removed by washing the extract with aqueous sodium carbonate. The quasi-acid fraction (1 g.), a yellow gum, obtained by evaporation of the dried ethereal solution, gave an intense plum colour with ferric chloride. It did not give a semicarbazone and, since the quantity was too small for successful distillation, it was extracted with dry ligroin (b. p. 40—60°). Evaporation of the ligroin solution gave a colourless, very viscous gum (ferric chloride coloration), which was analysed after removal of the last trace of solvent in a high vacuum (Found : C, 53·2; H, 6·3. $C_{12}H_{16}O_7$ requires C, 52·9; H, 5·9%).

*Reduction of Methyl α-Bromo-*n*-propane-ααβ-tricarboxylate.*—An attempt was made to convert this ester into the $\Delta^{\alpha}$-propene ester by the action of silver hydroxide. No apparent action occurred when moist silver oxide, prepared from 15 g. of silver nitrate, was stirred with a solution of 17 g. of the bromo-ester in aqueous methyl alcohol at room temperature. The mixture was therefore refluxed for 6 hours, the silver bromide filtered off, and the filtrate poured into brine and extracted with ether. Distillation of the residue from the dried ethereal extract gave (together with products containing bromine) a main fraction, b. p. 132°/3 mm.—139°/2 mm., which crystallised and was identified as methyl *n*-propane-ααβ-tricarboxylate, m. p. and mixed m. p. 48°, reduction of the bromo-ester having taken place.

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