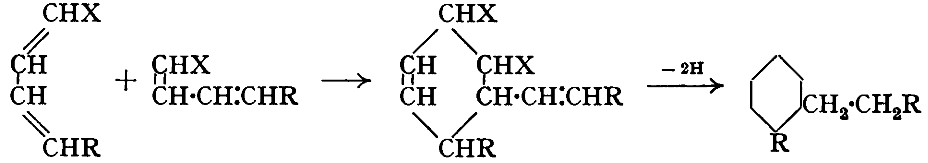
254. *Mechanism of Polymerisation. Part VI. Heat Polymerisation of Methyl Sorbate, and the Constitution of the Dimeric Products.*

By Ernest Harold Farmer and Colin R. Morrison-Jones.

When heated to 230° in the absence of air, methyl sorbate gives a mixture of low-molecular polymerides consisting mainly of dimerides and trimerides. The dimeric portion has been found to consist in part of the esters of three, or possibly four, difficultly crystallisable dimerides of sorbic acid, but principally of the ester of a liquid acid which itself doubtless consists of one or more additional dimeric forms.

The structural character of three homogeneous crystalline dimeric acids has been determined, and all three acids have proved to be dialkyl*cyclo*hexenedicarboxylic acids. The liquid dimeric acid, which has been little investigated, is probably closely related to the solid acids in constitution.

In the expectation of obtaining butadienoid hydrocarbons Doebner (*Ber.*, 1902, **35**, 2129; 1907, **40**, 146) distilled several diene acids of the formula R·CH:CH·CH:CH·CO_2H (R = H, Me, Ph) with anhydrous barium hydroxide. The distillates were not butadienes, but stable unreactive hydrocarbons apparently of formula $C_8H_{10}R_2$, all doubtless derived by decarboxylation of the dimerides of the respective acids. Kuhn and Deutsch (*Ber.*, 1932, **65**, 43) have since repeated Doebner's work with two of the acids (R = H, Me), and have shown that the products are not homogeneous, but consist in each case largely of a hydrocarbon of the formula $C_8H_8R_2$; and they have recognised that the volatile products from β-vinylacrylic acid and sorbic acid are ethylbenzene and *o*-propyltoluene respectively, these being formed presumably by polymeric addition reactions of Diels–Alder type, followed (under the drastic conditions of the reaction) by dehydrogenation and decarboxylation of the adducts :



(X = CO_2H)

A knowledge of the course of heat polymerisation in the simplest conjugated and unconjugated polycarboxylic acids has been of considerable interest in connexion with the determination of the polymerisation mechanism of the various types of drying oils, especially those of heat-treated or " thickened " drying oils, and in the present paper the result of heating a conjugated acid, *viz.*, sorbic acid, in the form of its methyl ester is described.

Polymerisation of methyl sorbate was found to occur readily when it was heated in carbon dioxide at atmospheric pressure between its boiling point (180°) and 230°. In the course of several hours' heating the ester thickened to give a viscous oil, which by fractional distillation at reduced pressure could be cleanly separated into monomeric, dimeric, and higher polymeric fractions. The last of these fractions (13% of the whole), a very viscous material, although doubtless capable of being separated into its polymeric grades by evaporative distillation, has not yet been closely investigated : the lower-boiling portion of it, however, definitely consisted of trimeric material, and the molecular weight of the whole fraction was such that only a small percentage of it could have been composed of tetrameric or higher-molecular material. The monomeric material recovered after the heat-treatment (6% of the whole) was not homogeneous : it consisted very largely of unchanged sorbic ester, but some small proportion of it had undergone heat alteration of a type which has not been determined.

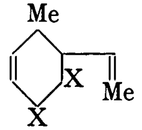
Distillation of the dimeric portion (81% yield) showed it to be heterogeneous, but very prolonged efforts to separate the components by using columns of different types proved abortive, and, of course, fractional evaporative distillation was unavailing owing to the isomeric character of the components. The best result finally obtained came from the systematic fractionation of large stocks of the dimeric fractions at 3·5 mm. pressure under jacketed Dufton-type columns fitted for close reflux control. In this way two constant-boiling mixtures (A) and (B) were separated from the main bulk of material, and these, unlike the unfractionated dimeride, gave some proportion of solid acid on hydrolysis.

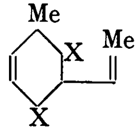
The mixture (A) absorbed 2 mols. of hydrogen on reduction, and showed the normal molecular refraction for a diene. It gave on hydrolysis with alkali an acid mixture containing three distinct crystalline acids (m. p.'s 216°, 210°, and 191°) and a fourth crystalline acid (m. p. 164—169°) isolated in very small yield and in doubtfully homogeneous condition, and over and above these a semi-resinous acid which accounted for 75—80% of the total hydrolysis product. The main structural characteristics of the first three acids have been determined, but the last two require further investigation.

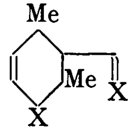
The three pure acids have been found to be monocyclic, dibasic, diolefinic acids, each having the formula $C_{12}H_{20}O_4$; moreover, one double bond in each of these acids is with little doubt endocyclic and the other extracyclic, since the two double bonds in each undergo reduction at greatly different rates. The saturated reduction product from each of these dimeric acids is heterogeneous, being composed of a mixture of crystalline isomerides in which one acidic form greatly preponderates.

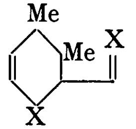
Dimeric Acid, m. p. 216°.—Dehydrogenation of this *substance* with selenium or palladised charcoal proceeded readily at 200—300°, the product with either reagent being an *acid*, $C_{12}H_{14}O_4$ (m. p. 178°), which gave mellophanic acid (benzene-1 : 2 : 3 : 4-tetracarboxylic acid) on vigorous oxidation with permanganate. In one dehydrogenation experiment, however, there was found, accompanying the usual product (m. p. 178°), a second acid, and this gave by oxidation and subsequent esterification a tetramethyl ester, $C_{15}H_{14}O_9$, which differed in composition from methyl mellophanate by the (additional) elements CO.

It is thus clear that the dimeric acid of m. p. 216° is a *cyclo*hexenic compound having with reasonable certainty groups attached at 1 : 2 : 3 : 4-positions in the ring. Now the four structures (I)—(IV), products of a Diels–Alder type of dimerisation, would all normally give mellophanic ester if dehydrogenated and then oxidised; all, moreover, would contain one endocyclic and one extracyclic double bond. Discrimination between substances having these structures might be expected to be achieved by means of oxidation with permanganate, but this expectation would be diminished if the ring double bond were displaced towards either the methyl group or the carbonyl group, owing to the strong tendency which the molecule would then show to break down progressively under oxidation (or even by hydrolysis after the initial stage of oxidation had occurred) to oxalic acid, acetic acid, and carbon dioxide. Actually, the dimeride of m. p. 216° gave oxalic acid progressively throughout its oxidation with permanganate, and this, together with acetic acid, were the only products of reaction; if, however, the oxidation were interrupted and the intermediate products heated at 100° in acid solution much oxalic acid was formed by hydrolysis. Clearly then the ring double bond was not in the position shown in formulæ (I)—(IV).

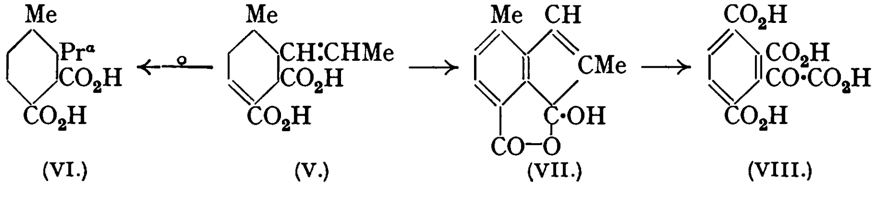

(I.)


(II.)

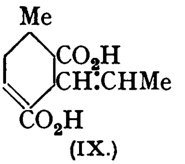

(III.)


(IV.)

Ozonolysis of solutions of the dimeric acid, followed by oxidation of the derived aldehydes with permanganate, gave usually only acetic acid, but eventually under different conditions very small yields of oxalic acid and a pentanetricarboxylic acid, m. p. 155°, were obtained. The latter acid was identified by synthesis as β-methylbutane-αβγ-tricarboxylic acid, but its isolation did not fix the constitution of the dimeride; it was discovered, however, that by ozonising the *solid* acid in suspension in chloroform and oxidising the hydrolysed ozonide with permanganate the products were then acetic acid (0·61 mol.), oxalic acid (a trace), and a tetracarboxylic acid, $C_9H_{12}O_8$, m. p. 169° (0·5 mol.), which lost carbon dioxide on heating to give the above-mentioned β-methylbutane-αβγ-tricarboxylic acid. Finally, it was found that a crystalline *anhydride* could readily be formed from the dimeric acid, so serving to confirm the presence of the two carboxyl groups on adjacent carbon atoms of the ring. The structure of the dimeric acid could then only be that shown in (V), and the tetrabasic oxidation acid was accordingly *β-methylbutane-αγδδ-tetracarboxylic acid.*


(VI.) (V.) (VII.) (VIII.)

It is clear from the above that the dimeric acid gave methylpropylphthalic acid (VI) by dehydrogenation, and mellophanic ester by oxidation of (VI), followed by esterification; it gave also by dehydrogenation an acidic by-product which could be converted by oxidation and subsequent esterification into an ester richer than mellophanic ester by the elements CO. It seems probable that the ester was *methyl* 3-*oxalylbenzene*-1 : 2 : 4-*tricarboxylate* (as VIII), arising through the formation and oxidation of an indene derivative (VII).



(IX.)

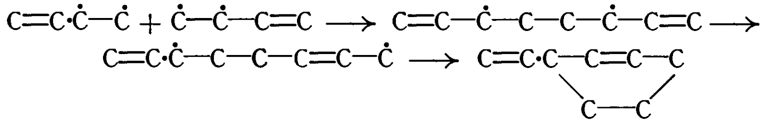
Dimeric Acid, m. p. 191°.—This dimeric *acid* gave the same end-products as did the foregoing acid when degraded by permanganate and by ozonolysis, but unlike that acid it did not yield an anhydride with acetyl chloride. On dehydrogenation it gave no recognisable amount of any aromatic acid; on the contrary it gave a hydrocarbon $C_6H_4{\cdot}C_4H_{10}$ which in turn yielded *iso*phthalic acid when energetically oxidised with permanganate. Thus the two original carboxyl groups of the dimeride had become eliminated during dehydrogenation, and the alkyl groups forming the side chains were clearly in *meta*-positions in the ring. These facts together showed that the constitution of this dimeric acid was (IX), the dehydrogenation product being *m*-propyltoluene.

Dimeric Acid, m. p. 200°.—Catalytic hydrogenation of this *dimeride* gave a mixture of tetrahydrides, but largely a crystalline acid, m. p. 164°, which proved to be identical with one of the two solid tetrahydrides derived from the dimeric acid, m. p. 191°. Consequently, this dimeric acid (m. p. 200°) resembles its isomeride of m. p. 191° (IX) in essential structure, and differs from it either in the position of a double bond (doubtless the ring double bond) or by *cis-trans*-stereoisomerism. Which of these possibilities is correct has not been determined, but prolonged boiling of the dimeride with potassium hydroxide failed to promote conversion (αβ, βγ) into its isomeride of m. p. 191°, so that its representation by the βγ-double-bonded formula corresponding to (IX), *i.e.*, (II), seems unlikely to be correct.

Liquid Dimeric Acid.—This major product of the dimerisation reaction, doubtless still containing small amounts of the foregoing crystalline acids, has only been superficially investigated, and it is therefore uncertain whether, apart from the residual traces of the crystalline acids, it represents one, or more than one, dimeric form. The fact that this form of the dimeride is liquid, or at least very slow to crystallise, does not (in the light of experience with other isomeric dimerides) by any means necessarily denote a departure from the *cyclo*hexenic constitution; and indeed, such preliminary oxidation experiments as we have carried out indicate that it has such a constitution.

The constant-boiling mixture (B) also gave rise on hydrolysis to small amounts of one or more of the foregoing crystalline dimeric acids, but the major portion of the hydrolysis product was a liquid acid which has not been closely examined.

With regard to the mechanism of formation of the *cyclo*hexenic dimerides the striking feature of the results is the addition of the CH:CH·CO group of one reacting molecule across the terminals of the usually strongly polarised diene system $CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH$ *in both of the possible directions*. It is not surprising, in view of the ease with which Diels–Alder reactions are normally effected, that the CH:CH·CO· group rather than the $CH_3{\cdot}CH{:}CH{\cdot}$ group of sorbic acid functions as the reactive part of the addendum molecule, but the results above described make it clear that, if the initial molecular activations are strictly polar in character, then *both* of the polarised forms $CH_3{\cdot}\overset{+}{C}H{:}CH{\cdot}CH{:}\overset{-}{C}H{\cdot}CO$ and $CH_3{\cdot}\overset{-}{C}H{:}CH{\cdot}CH{:}\overset{+}{C}H{\cdot}CO$ must be available at the moment of reaction and participate in the addition. This being so, it seems likely that the course of reaction in this thermal polymerisation is dependent on the formation of free-radical forms of the monomeric molecules rather than polar ones, and follows essentially the course :



It may well be, then, that other dimeric forms derived by addition of the CH_3·CH:CH· unit of one sorbic acid molecule to the terminals of a second molecule are contained in the unidentified portion of the polymerisate.

Experimental.

Polymerisation of Methyl Sorbate by Heat.—Pure methyl sorbate (b. p. 69°/12 mm.; m. p. 4—5°; $n_D^{16°}$ 1·5066; $d_{4°}^{16°}$ 0·9620; $[R_L]_D$ 38·95, Σ 3·70) was heated in quantities of about 400 c.c. in a flask fitted with a gas inlet-tube, a Liebig condenser, and a thermometer dipping into the ester. Before the reaction was started, the air in the flask was displaced by carbon dioxide, and throughout the reaction a slow stream of this gas was bubbled through the ester. At first the flask was heated fairly rapidly but afterwards, when the ester began to boil (about 180°), heating was moderated. After 3 hours the contents of the flask had reached 230—235°, and by this time ebullition had ceased. The polymerised ester was allowed to cool in an atmosphere of carbon dioxide: it formed a yellow viscous oil smelling faintly of methyl sorbate.

Fractionation.—The first stage consisted in a rough separation of the polymerised ester into monomeric, dimeric, and mixed higher polymerides by fractional distillation at 3 mm. When the heat treatment had lasted 3½ hours (as above) there was 6% of monomeric material (b. p. below 110°), 81% of dimeric material (b. p. 110—150°), and 12% of a viscous oily residue which was mostly trimeric (*M*, in benzene, 351. Calc.: 378). When the total period of heat treatment was 2½ hours, the proportions of monomeric, dimeric, and crude trimeric material were 14, 75, and 10% respectively. Although a pure trimeric fraction could doubtless have been isolated from the crude trimeric portion by evaporative distillation, we were unable to undertake this work.

The monomeric fraction (*M*, in benzene, 121. Calc.: 126), smelling strongly of methyl sorbate, was a mobile yellow oil. It probably consisted mainly of methyl sorbate and readily gave a good yield of addition product with maleic anhydride; the somewhat inconstant b. p., however, indicated that the material was not entirely homogeneous.

The dimeric fraction was a fairly viscous colourless oil. Preliminary fractionation showed it to be a complex mixture of isomerides. A batch of 335 g. was therefore divided into 72 fractions in two successive fractional distillations at 3 mm., an Adams flask surmounted by a 10-inch Dufton column being used and the course of each distillation being followed by drawing refractive index–mass curves. The portions corresponding to the flats of the various curves were separately refractionated at 0·2 mm., a vacuum jacketed 22-inch column (½-inch diameter) with nichrome wire spiral, and a reflux ratio of 40 being used. The voluminous physical data accumulated in the various fractionations are omitted, but the curves indicated that certain fractions were alike in being composed of one apparently homogeneous dimeric ester, whilst another set of fractions were composed of a second dimeric ester. Investigation, however, of the hydrolysis products of these two materials showed that both were heterogeneous and were indeed no more than constant-boiling mixtures of dimerides. Nevertheless, their isolation led directly to the isolation of solid dimeric acids by hydrolysis. The first of these mixtures (Mixture A) had $d_{4°}^{18°}$ 1·062; $n_D^{18°}$ 1·47806; $[R_L]_D$ 67·07 (Calc. for $C_{14}H_{20}O_4$: 67·03), and the second (Mixture B) had $n_D^{17°}$ 1·49063. At a rough estimate the proportion of Mixture A (including fractions with refractive indices between 1·47720 and 1·47870) is 13%, and that of Mixture B (including fractions with indices above 1·49000) is 12% of the total dimeric material.

Constant-boiling Mixture A.—Hydrogenation. This heterogeneous dimeric ester absorbed 2·0 mols. of hydrogen (Adams's catalyst) in 8 hours. The *tetrahydride* was a colourless oil having b. p. 82—82·5°/0·1 mm., $n_D^{17°}$ 1·4594—1·4602, but consisting mostly of material having $n_D^{17°}$ 1·4598, $n_{4°}^{17°}$ 1·034, $[R_L]_D$ 67·82 (Calc.: 67·96) (Found: C, 65·65; H, 9·35. $C_{14}H_{24}O_4$ requires C, 65·60; H, 9·45%).

Hydrolysis. The Mixture A was heated in a steam-bath for 20—30 mins. with 10 times its weight of methyl-alcoholic potash. A solid potassium salt separated from the hot solution and gave on acidification an acid, m. p. 200—205° (5—9% yield). The filtrate yielded, on being worked up in the usual way, a pale yellow resinous acid which, after being dried over phosphoric oxide in a vacuum and taken up in benzene–petroleum, deposited a mixture of acids of m. p. 165—185° in the course of a few days (yield 12—15%). From the mother-liquor a considerable amount of a yellow oily acid was obtained by evaporation, and this deposited a little more of the solid mixture of acids but for the most part remained liquid. The constitution of this major (liquid) constituent of the mixed dimeric acids has not been determined.

The solid acid, m. p. 200—205°, was recrystallised 5 times (with 50% loss) from aqueous acetic acid or aqueous methyl alcohol and then gave short, thick, colourless needles, m. p. 216°

(with anhydride formation). This acid alone of the dimeric acids here described could be isolated (*via* the potassium salt) in nearly pure condition directly, after hydrolysis, from the once-fractionated dimeric ester. It was 1-*methyl*-2-*propenyl*-Δ^{4}-cyclo*hexene*-3 : 4-*dicarboxylic acid* (Found : C, 64·2; H, 7·15; equiv., 111·7; *M*, in acetic acid, 220. $C_{12}H_{16}O_4$ requires C, 64·2; H, 7·2%; equiv., 112·1; *M*, 224·2).

Exhaustive fractional crystallisation from ether–petroleum of the solid residues left after separation of the acid, m. p. 216°, gave an isomeric dimeric acid, m. p. 200° (0·5% yield). This acid was, however, better obtained when Mixture A (10 g.) was refluxed for 16 hours with potassium hydroxide (5 g.) dissolved in 10 c.c. of water and 50 c.c. of methyl alcohol, and the resinous mixed acid so produced (freed from unhydrolysed material) directly taken up in ether, and the resulting solution rendered turbid with petroleum and afterwards allowed to stand for several weeks. The crystals deposited melted at 165—180°, and gave after repeated crystallisations, first from purified ethyl acetate and then from ether–petroleum, 0·7 g. of acid, m. p. 200°. Mixed m. p. with dimeric acid of m. p. 216°, 175—185°, and with dimeric acid of m. p. 191° (see below), 162—170°. This acid, 1-*methyl*-3-*propenyl*-Δ^{7}-cyclo*hexene*-2 : 4-*dicarboxylic acid* (Found : C, 64·0; H, 7·3; equiv., 111·5. $C_{12}H_{16}O_4$ requires C, 64·2; H, 7·2%; equiv., 112·1), dissolved in boiling water and was sparingly soluble in ethyl acetate and in ether; its potassium salt was soluble in methyl alcohol.

The mixed acids, m. p. 168—185°, from the methyl alcohol-soluble potassium salts when fractionally crystallised from purified ethyl acetate or from ether–petroleum yielded opaque or transparent prisms, m. p. 191° (mixed m. p. with dimeric acid of m. p. 216°, 165—175°). This acid, 1-*methyl*-3-*propenyl*-Δ^{4}-cyclo*hexene*-2 : 4-*dicarboxylic acid*, dissolved sparingly in ether and ethyl acetate but not in chloroform or cold water (Found : C, 64·25; H, 7·25; equiv., 111·1; *M*, in benzene, 230. $C_{12}H_{16}O_4$ requires C, 64·2; H, 7·2%; equiv., 112·1; *M*, 224·2).

By repeated fractional crystallisation from ethyl acetate and from ether–petroleum of the solid residues from the acid, m. p. 191°, a further amount of the latter acid was first obtained, and ultimately an acid, m. p. 164—169°, which could not be subdivided by further crystallisation. This acid appeared to represent a fourth crystalline dimeric acid, but its homogeneity has not been adequately confirmed or its constitution determined (Found : C, 64·1; H, 7·1%).

Constant-boiling Mixture B.—This mixture (3 g.) was hydrolysed by refluxing for 30 mins. with 1·5 g. of potassium hydroxide dissolved in 40 c.c. of methyl alcohol. The product did not deposit a crystalline potassium salt but, on being worked up, yielded a resinous acid which swelled to a brittle froth when dried over phosphoric oxide in a vacuum, but congealed to a hard mass in moist air. When the dry acid was dissolved in benzene, and the solution diluted to the point of turbidity with petroleum, it deposited over several weeks crystals, m. p. 169—184°. These were found by slow recrystallisation from ether–petroleum to contain a little of the dimeric acid (0·1 g.) of m. p. 216°, but the nature of the major portion has not yet been determined.

The *dianilide* derived from Mixture B by interaction with anilinomagnesium bromide was partly solid and partly liquid. The solid portion separated from boiling methyl alcohol in fine needles, m. p. 288—290° (decomp.) (Found : C, 76·65; H, 6·95. $C_{24}H_{26}O_2N_2$ requires C, 76·95; H, 7·0%). This, however, could not be hydrolysed by prolonged boiling with methyl-alcoholic potash.

Dimeric Acid, m. p. 216°.—*Hydrogenation.* The acid, dissolved in 90% alcohol, absorbed in contact with Adams's catalyst 1 mol. of hydrogen rapidly, and a second mol. slowly (Found : 0·982 mol. and 1·994 mols. respectively). The reduced acid slowly solidified, and after recrystallisation from ether–petroleum formed colourless prisms, m. p. 188° (Found : C, 63·25; H, 8·85. $C_{12}H_{20}O_4$ requires C, 63·1; H, 8·85%). This was 1-*methyl*-2-*propyl*cyclo*hexane*-3 : 4-*dicarboxylic acid.* The mother-liquors contained a second acid (m. p., in crude form, 154—159°) which has not been further purified or examined.

Anhydride. Refluxed for 6 hours with acetyl chloride (25 c.c.), the dimeric acid (2 g.) gave an oily anhydride which solidified slowly when kept in a vacuum desiccator over potassium hydroxide and phosphoric oxide. The solid (1-*methyl*-2-*propyl*cyclo*hexane*-3 : 4-*dicarboxylic anhydride*) crystallised from ether–light petroleum in leaflets, m. p. 84°, or very slowly from the same solvent in needles, m. p. 84° (Found : C, 69·65; H, 6·65. $C_{12}H_{14}O_3$ requires C, 69·85; H, 6·85%). When boiled with water for a few minutes the anhydride reverted to the original acid, m. p. 216°.

Dehydrogenation. When heated for 18 hours in a carbon dioxide atmosphere with an equal weight of selenium, the acid (2 g.) underwent smooth dehydrogenation. In the early stages the anhydride of the acid (m. p. 84°) refluxed up the condenser; ultimately a brown oil was formed which, by extraction with ether and subsequent boiling with water (to convert anhydrides into acids), yielded an oil which slowly solidified when left over phosphoric oxide in a vacuum desiccator. The solid acid so obtained was triturated with cold benzene–light petroleum and crystallised from the same mixed solvent; it formed fine white prisms, m. p. 178° (with anhydride formation); yield: 0·7 g. (Found: C, 64·8, 64·75; H, 6·45, 6·35; equiv., 113·4. $C_{12}H_{14}O_4$ requires C, 64·8; H, 6·35%; equiv., 111·1). The same *acid* (m. p. 178°) was obtained when the dimeric acid was dehydrogenated at 290—305° for 6 hours in presence of 5% palladised charcoal.

Oxidation of the dehydrogenation product. The acid (0·4 g.) was refluxed with 100 c.c. of 5% aqueous permanganate for 18 hours, and the solution decolorised with the minimal amount of sulphur dioxide. The aqueous product, after acidification with hydrochloric acid, gave on continuous extraction with ether (16 hours) an acid, m. p. 224—227° (decomp.). This acid, which was almost insoluble in dry ether, could not be purified by recrystallisation: it was accordingly esterified at 0° in ether–methyl alcohol solution with diazomethane. The ester, when freed from solvent and triturated with a little cold methanol, solidified; the solid crystallised from methyl alcohol in fine needles, melting constantly at 129—130°. This ester was tetramethyl mellophanate (mixed m. p. with authentic specimen of m. p. 129—131°, 129—131°). In contact with air both the new and the authentic specimen acquired a faint purple colour.

When the crude selenium dehydrogenation product (see above) was extracted with ether, and the ethereal extract refluxed over sodium, a sodium salt separated. The salt gave on acidification and decolorisation with charcoal a crude crystalline acid, m. p. 167—169°. When this acid, without further purification, was oxidised with boiling permanganate solution as above, it gave an acid, m. p. 212—216° (decomp.); this product on esterification with diazomethane gave an ester, m. p. 97—99°, which by fractional crystallisation from methanol was resolved into (1) an ester, m. p. 102° (colourless prisms), and (2) methyl mellophanate, m. p. 128—130°. The ester, m. p. 102°, had the empirical formula $C_{15}H_{14}O_9$, and appeared to be *methyl* 3-*oxalylbenzene*-1 : 2 : 4-*tricarboxylate* (as VIII) (Found: C, 53·5, 53·3; H, 4·15, 4·3. $C_{15}H_{14}O_9$ requires C, 53·2; H, 4·15%).

Ozonolysis. When ozonised in purified ethyl acetate, the dimeric acid (2 g.) gave a syrupy ozonide. This was warmed with water (30 c.c.), and the product first basified with sodium carbonate [*] and then oxidised at 0° with 5% permanganate solution (40 c.c.). The oxidation liquor was just decolorised with sulphur dioxide, then acidified, and finally continuously extracted with ether for 24 hours. The extract on removal of ether and distillation gave (1) acetic acid, isolated as silver salt (colourless needles, 0·25 mol. Found: Ag, 64·2. Calc.: Ag, 64·6%), (2) a trace of oxalic acid, m. p. 101°, and (3) an oily acid which after standing for several weeks over phosphoric acid largely solidified. This last acid, which crystallised in characteristic colourless prisms, m. p. 155°, from chloroform–light petroleum, was identified as β-methylbutane-αγδ-tricarboxylic acid (mixed m. p. with authentic acid [†] of m. p. 155°, 155°; mixed m. p. with authentic α-ethyltricarballylic acid [‡] of m. p. 156°, 138—142°) (Found: C, 47·4; H, 5·8; equiv., 68. Calc. for $C_8H_{12}O_6$: C, 47·05; H, 5·95%; equiv., 72).

When the finely-powdered acid (1·65 g.) was ozonised for 3 hours in suspension in chloroform, a solid ozonide was formed as a flocculent precipitate. This was rapidly removed, dissolved in water (30 c.c.), and freed from unchanged acid (0·05 g.) by filtration. The aqueous filtrate was neutralised with sodium carbonate and oxidised at 0° with 5% permanganate solution (28 c.c.). The product yielded acetic acid (isolated as silver acetate, 0·61 mol.), a little oxalic acid, and an oily polybasic acid. The last largely solidified on standing over phosphoric oxide in a vacuum desiccator; the solid (0·65 g.) was recrystallised (with difficulty) first from ether–benzene and then from ether–benzene–petroleum. It melted with loss of carbon dioxide at 169° (Found: C, 43·45; H, 4·8; equiv., 62·9. $C_9H_{12}O_8$ requires C, 43·5; H, 4·9%; equiv., tetrabasic, 62·0). The product formed when this acid was heated at 180° for a few minutes was a yellow oil which, when left in solution in chloroform–light petroleum, gave very slowly the characteristic crystals of β-methylbutane-αγδ-tricarboxylic acid, m. p. 155°. The tetrabasic acid, m. p. 169°, was thus β-*methylbutane-αγδδ-tetracarboxylic acid.*

Oxidation with permanganate. A solution of the acid (2·5 g.) in water (20 c.c.) was just

[*] If the solution was made strongly alkaline with potassium hydroxide, the yield of acetic acid was reduced, that of oxalic acid was increased, and no methylbutanetricarboxylic acid at all was obtained.

[†] Synthesised by the method of Hope and Perkin, J., 1911, **99**, 766.

[‡] Synthesised by the method of Jowett, J., 1901, **79**, 1348.

neutralised with sodium carbonate and oxidised at 0° with 5% potassium permanganate (230 c.c. decolorised). The product was filtered, and the filtrate and manganese mud washings rendered faintly acid and then concentrated on a steam-bath. The concentrate was continuously extracted with ether for 24 hours, but the extract yielded only some acetic acid (much had evaporated during the concentration) and oxalic acid (0·52 g.).

A similar experiment, in which the oxidation liquor was freed from manganese mud by sulphur dioxide, and the cold dilute acidic liquor immediately extracted with ether, gave 0·26 mol. of acetic acid and a mere trace of oxalic acid. Hence, in neither experiment did any tribasic acid survive, and the oxalic acid was evidently formed readily by hydrolytic fission of the oxidised dimeride. This behaviour agrees with that to be expected from a dimeride of formula (V).

Dimeric Acid, m. p. 191°.—*Hydrogenation.* The acid, dissolved in alcohol, absorbed 2 mols. of hydrogen (Found : 1·99 mols.) in presence of Adams's catalyst, but the difference in the rate of absorption of the first mol. and the second was less marked than with the preceding dimeride. The oily tetrahydride slowly solidified : it formed colourless prisms, m. p. 164°, from ether–light petroleum (Found : C, 63·15; H, 8·9. $C_{12}H_{20}O_4$ requires C, 63·1; H, 8·85%), and was *4-methyl-2-*n*-propyl*iso*phthalic acid.* The evaporated mother liquors yielded a second (crude) acid, m. p. 145—150°, which has not been examined.

Action of acetyl chloride. When the dimeric acid was boiled with excess of acetyl chloride for 6 hours the product consisted of unchanged acid and an unsolidifiable oily material from which no anhydride could be isolated.

Dehydrogenation. When dehydrogenated by heating with selenium under the conditions described above, the dimeride showed no signs of passing first into its anhydride. After the heating had continued for 18 hours at 210—220°, the product was a brown mobile liquid which when worked up and distilled gave a colourless mobile fraction, b. p. 170—190°. This product gave on oxidation with excess of boiling permanganate a white acidic powder, m. p. 324—328° (decomp.), which was recognised as crude *iso*phthalic acid; the methyl ester of this acid, formed by the action of ethereal diazomethane, crystallised from alcohol in fine needles, m. p. 65—66° (mixed m. p. with authentic ester, 65—66°).

Ozonolysis. The finely-powdered acid was ozonised in chloroform at 0° for 1½ hours. The solid ozonide was filtered off, dissolved in water, and a small residue of unchanged acid filtered off. The neutralised aqueous filtrate was oxidised at 0° with 5% permanganate, and the product worked up as before. Acetic acid was isolated in the form of silver acetate (0·34 mol.), and from the residue a polybasic acidic oil was obtained which was crystallised by dissolving it in benzene containing a trace of ether and keeping the solution for several days. The crystals after being twice recrystallised from benzene–light petroleum melted at 169° (decomp.) and not only gave no depression of m. p. with the β-methylbutane-αγδδ-tetracarboxylic acid of m. p. 169° obtained by ozonolysis of the dimeric acid of m. p. 216°, but like this acid of m. p. 169° readily underwent decarboxylation at 180° to give β-methylbutane-αγδ-tricarboxylic acid, m. p. 155° (mixed m. p. 155°). The crystallisation liquors yielded a little oxalic acid, m. p. 101°, on dilution with petroleum.

Oxidation with permanganate. Oxidation at 0° with 5% aqueous permanganate proceeded similarly to that observed with the dimeric acid of m. p. 216°, and the (progressively produced) products were again acetic acid and oxalic acid unaccompanied by a solid polybasic acid.

Dimeric Acid, m. p. 200°.—*Hydrogenation.* The acid, dissolved in alcohol, absorbed 2 mols. of hydrogen (Found : 2·0 mols.) in presence of Adams's catalyst. The tetrahydride crystallised in colourless prisms, m. p. 164°, from ether–petroleum, and proved to be identical (mixed m. p. 164°) with the hydrogenation product of the same m. p. derived from the dimeric acid of m. p. 191°.

Action of alkali. In order to determine whether this dimeric acid was a βγ-isomeride of the dimeric acid of m. p. 191°, it was heated for 12 hours with excess of 10% methyl-alcoholic potash to induce equilibration. No isomerisation occurred.

Action of hydrochloric acid. The dimeric acid was heated with concentrated hydrochloric acid for 10 hours in a sealed tube at 160° to induce *cis-trans*-isomerisation. Much carbonisation occurred, but no isomeric acid could be isolated.

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IMPERIAL COLLEGE, LONDON, S.W. 7. [*Received, July* 17*th*, 1940.]