

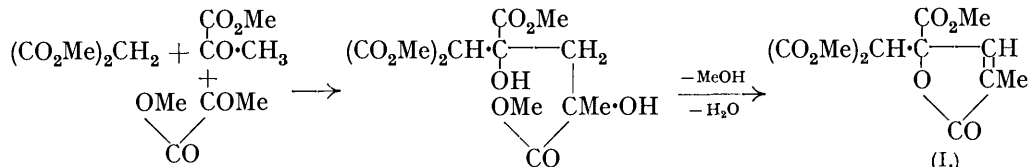
**272.** *Condensation of Methyl Pyruvate with Methyl Malonate in the Presence of Anhydrous Zinc Chloride.*

By JOHN W. BAKER and ANNIE S. LAUFER.

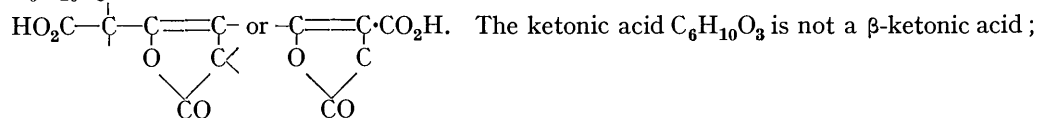
THE condensation between methyl pyruvate and methyl malonate in the presence of anhydrous zinc chloride was investigated in an attempt to effect a direct, one-stage synthesis of the ester  $\text{CO}_2\text{Me}\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{Me})_2$  (Baker, J., 1933, 811). The actual products of this condensation are of a more complex nature. From the neutral product was isolated a highly crystalline material, m. p.  $119^\circ$ , of composition  $\text{C}_{12}\text{H}_{14}\text{O}_8$ , which is therefore derived by condensation between 2 mols. of methyl pyruvate and 1 mol. of methyl malonate with the elimination of 1 mol. each of water and methyl alcohol. The ester is unsaturated and exhibits reducing properties. Preliminary investigation revealed the

presence of three carbomethoxy-groups and a lactone ring, and suggested that it is probably a  $\Delta^{\alpha}$ -unsaturated  $\gamma$ -lactonic ester. Representatives of this class are not common, and a study of its reactions was considered to be of interest, especially since a closely similar system is present in the cardiac aglucones.

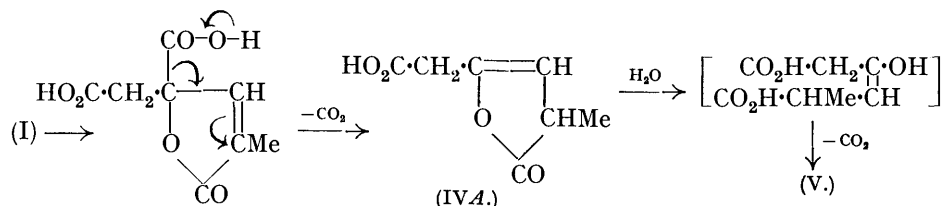
On the basis of the reactions recorded below, it is concluded that the substance  $C_{12}H_{14}O_8$  is *methyl 2-keto-3-methyl-2 : 5-dihydrofuran-5-malonate-5-carboxylate* (I), the formation of which from the pyruvic and malonic esters can be readily represented by the scheme



Hydrolysis of (I) with 50% aqueous potassium hydroxide under mild conditions converts it into a *methyl dihydrogen ester*. This must possess the structure (II), the carbomethoxy-group attached to the quaternary carbon remaining unhydrolysed. It is a malonic acid, and is converted by heating at its melting point into the *methyl hydrogen ester* (III), with loss of carbon dioxide. Hydrolysis of this new ester with hot concentrated hydrochloric acid causes fission of the 5-carbomethoxy-group to give *2-keto-3-methyl-2 : 5-dihydrofuran-5-acetic acid* (IV), which, in agreement with the structure assigned, affords only a *mono-methyl ester*, b. p.  $126^\circ/1 \text{ mm.}$ , when treated with diazomethane. The same acid is obtained by direct hydrolysis of the ester (I) with concentrated hydrochloric acid, but, under these conditions, a considerable quantity of a liquid keto-acid,  $C_6H_{10}O_3$  (V), is also formed. The simultaneous production of this keto-acid suggests that the hydroxyl group, introduced by the opening of the lactone ring in the lactonic acid  $C_7H_8O_4$ , is capable of ketonisation, to produce a  $\beta$ -keto-acid, which then loses a molecule of carbon dioxide to give the acid  $C_6H_{10}O_3$ . This hypothesis requires the presence in the precursor of the grouping

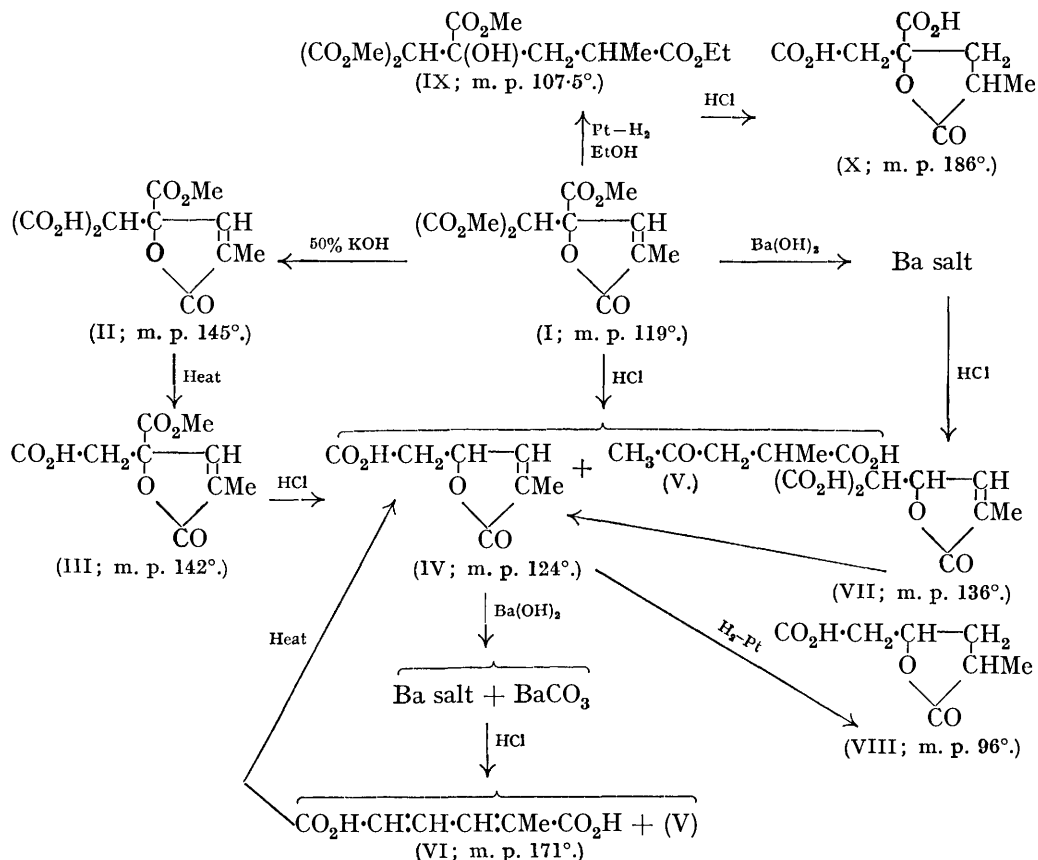


hence the number of possible isomerides is not large. Systematic synthesis of the possible structures showed the liquid keto-acid to be identical with  $\alpha$ -methyl-lævulic acid, obtained by acid hydrolysis of *methyl  $\beta$ -acetyl- $\alpha$ -methylsuccinate*, the condensation product from methyl  $\alpha$ -bromopropionate and methyl sodioacetoacetate. The keto-acid is apparently derived from a 2 : 3-dihydrofuran structure (IV.A) which, in theory, could be obtained by prototropic change from the 2 : 5-dihydro-acid (IV). In this system, however, the 2 : 5-dihydro-compound should be the favoured isomeride, since the polar effect of the 3-methyl group would be to stabilise the double bond in the  $\alpha\beta$ -position.\* Actually, no trace of the keto-acid can be detected when the pure lactonic acid (IV) is heated with concentrated hydrochloric acid, and it must, therefore, be concluded that the considerable amount formed during the similar hydrolysis of the parent ester (I) is derived from the 2 : 3-dihydro-acid which results from the extrusion of carbon dioxide necessary to provide the requisite hydrogen atom for prototropic mobility in the potential three-carbon system :



\* It is of interest, however, that the acid (IV) gives a positive Legal test, which Jacobs, Hoffmann, and Gustus (*J. Biol. Chem.*, 1926, **70**, 1) found to be typical of  $\beta\gamma$ -unsaturated  $\gamma$ -lactones having an  $\alpha$ -hydrogen atom. In accordance with their conclusions, neither the ester (I) nor the saturated lactonic acid (VIII) gives a positive reaction.

Confirmation of this view is provided by the hydrolysis of the acid (IV) with boiling barium hydroxide solution. Precipitation of barium carbonate indicates the elimination of a carboxyl group, and back-titration shows that 2—3 equivs. of baryta have been used. Acidification of the soluble barium salt gives an unsaturated acid (VI), isomeric with (IV), and the keto-acid  $C_6H_{10}O_3$ . The greater mobility of the prototropic system in the presence of the alkaline reagent evidently permits the formation of the unsaturated lactonic acid (IV.A) from which the keto-acid is derived. Unlike its precursor, the unsaturated acid (VI) is dibasic but is reconverted into the lactonic acid (IV) when it is heated at its melting point: (VI) is therefore most probably  $\alpha$ -methylmuconic acid, formed by ethylenic elimination of water from the intermediate hydroxy-acid. Its conversion into the lactonic acid



when heated is exactly comparable to the similar conversion of  $\beta$ -methylmuconic acid into 2-keto-4-methyl-2:5-dihydrofuran-5-acetic acid (Pauly and Will, *Annalen*, 1917, **416**, 1). An attempt was made to synthesise  $\alpha$ -methylmuconic acid by the action of concentrated alcoholic potassium hydroxide upon the product of dibromination of  $\alpha$ -methyladipic acid. The resulting acid, m. p. 276° (decomp.), gave the correct analytical figures and is evidently the high-melting form, since it was reduced to  $\alpha$ -methyladipic acid. The acid obtained by hydrolysis of the lactonic acid (IV) is probably the low-melting form, although with the small amount of material available no pure crystalline material could be isolated from its reduction product. Hydrolysis of the original ester (I) with boiling barium hydroxide solution gives a crystalline *barium* salt, from which is obtained 2-keto-3-methyl-2:5-dihydrofuran-5-malonic acid (VII). This, in agreement with the structure assigned, is converted into the 5-acetic acid (IV) at its melting point.

Reduction of the unsaturated lactonic acid with hydrogen and a platinum-black catalyst

converts it into *2-keto-3-methyltetrahydrofuran-5-acetic acid* (VIII). Saturation of the ethylenic bond destroys the prototropic system present in (IV) and thus precludes the possibility of the formation of the open-chain keto-acid by alkaline hydrolysis. In agreement with this it was found that only 2 equivs. of baryta were neutralised in the complete hydrolysis of the dihydro-acid.

Catalytic reduction (Adams) of the original ester proceeds smoothly in alcohol, but between 3 and 4 atoms of hydrogen are absorbed. Analysis of the product, however, agrees well with the composition of a *dihydro*-derivative which has added on one molecule of ethyl alcohol. The nature of this addition is uncertain, especially since the original unsaturated derivative (I) crystallises unchanged from hot alcohol, but it is considered probable that addition has occurred with rupture of the lactone ring to give *methyl β-hydroxy-δ-carbethoxy-n-pentane-ααβ-tricarboxylate* (IX). Hydrolysis of this ester with concentrated hydrochloric acid affords the normal dihydro-derivative *2-keto-3-methyltetrahydrofuran-5-acetic-5-carboxylic acid* (X). The retention of the 5-carboxyl group in the hydrolysis of the dihydro-ester, contrasted with its elimination when the acid hydrolysis precedes the reduction (to give the acid VIII), indicates that such elimination must be associated with the presence of the unsaturated lactone structure.

Attempts to elucidate the structure of the ester (I) and its hydrolysis product (IV) by ozonolysis were only partly successful. Formaldehyde and a little oxalic acid were the only identified products when the ozonide of (I) was decomposed by cold water. Formaldehyde was also detected in the volatile products obtained by the decomposition of the ozonide of (IV) by boiling water, and the acid portion, obtained by further oxidation with perhydrol in sodium bicarbonate solution, contained formic acid. In one experiment a very small yield of an acid, m. p. 118°, was isolated. It depressed the m. p. of the original acid (IV) and of methylsuccinic acid, and there is little doubt (see p. 1348) that it was slightly impure *dl*-malic acid. The isolation of this large fragment of the carbon skeleton of (IV) is strong confirmation of the correctness of the structure assigned.

The inter-relationships of these various derivatives are summarised in the scheme on p. 1344.

#### EXPERIMENTAL.

*Condensation of Methyl Pyruvate with Methyl Malonate.*—Various methods described in the literature for the esterification of pyruvic acid were tried, but most satisfactory results were obtained by use of the alcohol-vapour method without a catalyst, care being taken, by use of an efficient column, to prevent entrainment of the ester. Fractionation of the product obtained by passage of about 2 l. of methyl alcohol into 100 g. of pyruvic acid afforded approximately 30 g. of the ester, b. p. 132—136°. Attempts to oxidise methyl lactate directly to methyl pyruvate with selenium dioxide were unsuccessful.

*Methyl 2-Keto-3-methyl-2 : 5-dihydrofuran-5-malonate-5-carboxylate* (I).—Although this ester is derived from 2 mols. of methyl pyruvate and 1 mol. of methyl malonate, only a small yield is obtained when the esters are used in this ratio : much improved yields are obtained by using equimolecular quantities. A mixture of 42 g. of methyl pyruvate, 39 g. of methyl malonate, and 40 g. of powdered anhydrous zinc chloride was heated on the steam-bath for 2 hours. The yellow, viscous reaction mixture was cooled, poured into water, and the neutral products isolated by ether extraction in the usual manner. The concentrated ethereal solution deposited crystals (approx. 9 g.) which, recrystallised from dilute alcohol, gave the *ester*, m. p. 119° (Found : C, 50·4, 50·5; H, 5·0, 5·0; OMe, 32·35; M, 260, 262, 265. C<sub>13</sub>H<sub>14</sub>O<sub>8</sub> requires C, 50·35; H, 4·9; 3OMe, 32·5%; M, 286). Hydrolysis with 0·0457*N*-baryta and back-titration of the excess gave equiv. 72·4 (Calc. for 4CO<sub>2</sub>H : equiv., 71·5). The ester rapidly decolorises Baeyer's reagent, and readily reduces boiling Fehling's solution and ammoniacal silver nitrate. It was recovered unchanged from attempts to condense it with piperonal, *o*-phenylenediamine, phenyl-carbimide, and semicarbazide, or from interaction with diazomethane, and it would not form an acetyl derivative. Attempted methylation with methyl-alcoholic sodium methoxide and methyl iodide at atmospheric pressure afforded unchanged material as the only crystalline product. When the same reagents, with a large excess of methyl iodide, were heated in a sealed tube at 100°, the neutral product consisted of a yellow liquid which could not be induced to crystallise and was not examined further.

Repeated fractional distillation of the viscous yellow mother-liquor from which the ester

(I) had separated gave unchanged methyl malonate, and a pale yellow unsaturated liquid ester, b. p. 101°/0.6 mm. Analysis of this agrees with the composition  $C_{14}H_{20}O_8$ , but investigation of this product is only in the preliminary stages [Found: C, 50.5; H, 6.15; OMe, 37.8.  $C_{10}H_8O_5(OCH_3)_4$  requires C, 50.6; H, 6.03; OMe, 37.4%].

*Hydrolysis of (I).*—(a) *With potassium hydroxide.* The yellow solution obtained by dissolving 2 g. of the ester in 10 c.c. of 50% aqueous hydroxide was warmed to 80° on the steam-bath for a few minutes, cooled to 0°, extracted with ether, and the aqueous mother-liquor acidified with concentrated hydrochloric acid at 0°. The residue from the dried ethereal extract crystallised. Crystallisation from dry ether containing a few drops of chloroform gave the *methyl dihydrogen ester (II)*, m. p. 145° (decomp.) (Found: C, 46.5; H, 3.9; OMe, 11.85; equiv., dibasic, 129.2.  $C_{10}H_{10}O_8$  requires C, 46.5; H, 3.9; OMe, 12.0%; equiv., 129). The ester was heated at 145° until gas evolution ceased, and the resulting yellow liquid was dissolved in aqueous sodium bicarbonate. After ether extraction of any non-acidic material, the acid was liberated by addition of concentrated hydrochloric acid at 0°. The residue from the dried ethereal extract crystallised from ether containing a little ligroin to give *5-carbomethoxy-2-keto-3-methyl-2:5-dihydrofuran-5-acetic acid (III)*, m. p. 144°, depressed to 120—125° by admixture with the ester (II) (Found: C, 50.5; H, 4.8; OMe, 14.6; equiv., monobasic, ca. 195.\*  $C_9H_{10}O_6$  requires C, 50.5; H, 4.7; OMe, 14.5%; equiv., 214).

(b) *With barium hydroxide.* 2 G. of the ester (I) were gently refluxed with 750 c.c. of approx. 0.05*N*-baryta for 1 hour, with exclusion of carbon dioxide. The precipitated *barium salt* was filtered from the hot solution and washed successively with water, alcohol, and ether (Found: Ba, 44.9;  $H_2O$ , loss at 150°/5 mm., 7.0.  $C_{16}H_{14}O_{14}Ba_3 \cdot 4H_2O$  requires Ba, 45.1;  $H_2O$ , 7.8%). The barium salt was added, with constant shaking, to concentrated hydrochloric acid at 0°, and the liberated acid was extracted with ether. The residue from the dried extract slowly crystallised. Crystallisation from ether-ligroin (b. p. 60—80°) gave *2-keto-3-methyl-2:5-dihydrofuran-5-malonic acid (VII)*, m. p. 136° (decomp.) (Found: C, 48.3; H, 4.1; equiv., by direct titration, 100.2; equiv., by back titration, 64.0.  $C_8H_8O_6$  requires C, 48.0; H, 4.0%; equiv., 100.0 and 66.6, respectively). When heated at 135—140° until gas evolution had ceased, this acid was converted into the 5-acetic acid (IV), m. p. and mixed m. p. 124°.

(c) *With concentrated hydrochloric acid.* The original ester (I) (5 g.) was heated on a steam-bath with 30 c.c. of concentrated hydrochloric acid until evolution of carbon dioxide had ceased (1—1.5 hours). The hydrochloric acid was evaporated on the steam-bath, and the residue evaporated several times with ether until a homogeneous solution in ether was obtained. After concentration, crystals of *2-keto-3-methyl-2:5-dihydrofuran-5-acetic acid (IV)* separated. After crystallisation from ether, the acid had m. p. 124° (Found: C, 54.25, 54.2, 54.2; H, 5.4, 5.2, 5.2; equiv., 157.2.  $C_7H_8O_4$  requires C, 53.9; H, 5.1%; equiv., monobasic, 156). The acid was converted by diazomethane in ether-chloroform solution into its *methyl ester*, b. p. 126°/1 mm. (Found: C, 56.3; H, 6.2; OMe, 18.9.  $C_8H_{10}O_4$  requires C, 56.5; H, 5.9; OMe, 18.2%).

Evaporation of the ethereal mother-liquor from which the lactonic acid had separated afforded a pale yellow syrup which was essentially  $\alpha$ -methyl-lævulic acid. It was characterised as its semicarbazone, m. p. 182° (decomp.) (Found: C, 45.3; H, 7.0; N, 22.3. Calc. for  $C_7H_{13}O_3N_3$ : C, 44.9; H, 7.0; N, 22.4%), and its *p-nitrophenylhydrazone*, m. p. 170° (Found: C, 54.6; H, 5.6.  $C_{12}H_9O_4N_3$  requires C, 54.35; H, 5.7%). It was converted (methyl alcohol-sulphuric acid) into its methyl ester, characterised as its *p-nitrophenylhydrazone*, m. p. 142° (Found: C, 55.9; H, 6.2.  $C_{13}H_{17}O_4N_3$  requires C, 55.9; H, 6.1%). All these derivatives gave no depression when admixed with specimens obtained from synthetic  $\alpha$ -methyl-lævulic acid (below).

*Synthesis of  $\gamma$ -Keto-acids  $C_6H_{10}O_3$ .*— $\beta$ -Methyl-lævulic acid. Distillation of the neutral product obtained by the action of 20 g. of methyl iodoacetate upon the sodium compound prepared from 2.3 g. of sodium in 50 c.c. of dry methyl alcohol and 13 g. of methyl methyl-acetoacetate gave *methyl  $\gamma$ -keto- $\beta$ -methyl-n-butane- $\alpha$ - $\beta$ -dicarboxylate*, b. p. 125—126°/11 mm. (Found: C, 53.85; H, 6.9.  $C_9H_{14}O_5$  requires C, 53.5; H, 7.0%). Its *semicarbazone*, m. p. 151° from dilute alcohol, only separates after the reaction mixture has been kept for several days (Found: C, 46.8; H, 6.7.  $C_{10}H_{17}O_5N_3$  requires C, 46.3; H, 6.6%). Hydrolysis of this ester with concentrated hydrochloric acid on a steam-bath until gas evolution ceases affords  $\beta$ -methyl-lævulic acid. The semicarbazone, m. p. 179—180° (decomp.), is depressed to 167° by admixture with that of the liquid keto-acid obtained by hydrolysis of the ester (I).

\* Most equivalents in this paper were determined with a few mg. of material, an ordinary analytical balance and a microburette being used, and are thus subject to an error of several units %.

*α-Methyl-lævulic acid.* Similar condensation of methyl acetoacetate and methyl  $\alpha$ -bromopropionate afforded *methyl ̢-keto-n-pentane-̢̣-dicarboxylate*, b. p. 128·5°/12 mm. (Found: C, 54·2; H, 7·2.  $C_9H_{14}O_5$  requires C, 53·5; H, 7·0%). Hydrolysis with concentrated hydrochloric acid gave  $\alpha$ -methyl-lævulic acid as a colourless syrup, readily characterised as its semicarbazone, m. p. and mixed m. p. 181° (decomp.) [Gault and Salomon, *Ann. Chim.*, 1924, **2**, 133, give m. p. 189° (corr.), but repeated crystallisation did not raise the m. p. above 182°]. Its *p*-nitrophenylhydrazone, m. p. and mixed m. p. 170°, and the *p*-nitrophenylhydrazone of its methyl ester, m. p. and mixed m. p. 142°, were identical with the corresponding derivatives of the keto-acid obtained by hydrolysis of the ester (I).

*Action of Aqueous Barium Hydroxide upon (IV).*—0·048 G. of the 5-acetic acid (IV) was refluxed with 20 c.c. of 0·0457*N*-barium hydroxide. Titration of the excess with standard hydrochloric acid showed that 17·72 c.c. of the baryta had been used, corresponding to 2·63 equivs. per mol. A larger-scale experiment, after filtration of the precipitated barium carbonate (equivalent to 63% elimination of one carboxyl group), removal of the excess baryta with carbon dioxide, and evaporation to dryness, gave a barium salt (Found: Ba, 39·7%) which was added to a small quantity of moderately concentrated hydrochloric acid (1 : 1) at 0°. The concentrated, dried ethereal extract deposited crystals of *α-methylmuconic acid*, m. p. 171°, after crystallisation from acetone-chloroform (Found: C, 54·3; H, 5·55; equiv., 74·3.  $C_7H_8O_4$  requires C, 53·9; H, 5·1%; equiv., dibasic, 78). The ethereal mother-liquors gave a gummy acid which readily yielded a semicarbazone, m. p. 179° (decomp.), raised to 180° by admixture with that of a synthetic specimen of  $\alpha$ -methyl-lævulic acid. A small quantity of the  $\alpha$ -methylmuconic acid was heated to its m. p. for a few minutes and then cooled. Crystallisation of the product first from acetone and then from ether gave an acid, m. p. 122°, raised to 124° by admixture with the 5-acetic acid (IV).

*Reduction of the Lactonic Acid (IV).*—The acid (0·2 g.) was shaken with hydrogen and platinum-black in alcohol under atmospheric pressure for some days, absorption being very slow. Filtration and evaporation of the solution gave the *dihydro-acid* (VIII), m. p. 96° with previous softening, after crystallisation from ether-chloroform (Found: C, 52·9; H, 6·6; equiv., by direct titration, 156·4; by back titration, 78.  $C_7H_{10}O_4$  requires C, 53·0; H, 6·4%; equiv., monobasic, 158; dibasic, 79).

*Reduction of the Ester (I).*—The ester (1·43 g.) was suspended in about 80 c.c. of 96% alcohol and reduced with hydrogen, 0·1 g. of platinum oxide being used as catalyst. Absorption of approximately 1 mol. of hydrogen (133 c.c.) occurred during the first 6 hours, but overnight a further 80 c.c. were absorbed. The solution was warmed to dissolve all the product, filtered, concentrated to a very small bulk, and left to crystallise in the refrigerator. After draining on porous porcelain, the *ester* (IX) crystallised from ether in rosette clusters of short prisms, softening 105°, m. p. 107·5° (Found: C, 50·6; H, 6·0.  $C_{14}H_{22}O_9$  requires C, 50·3; H, 6·6%.  $C_{12}H_{16}O_8$  requires C, 50·0; H, 5·55%). A mixture of the reduction product and the original ester melted at 104—108°. 0·15 G. of this ester was heated with 5 c.c. of concentrated hydrochloric acid for 2 hours and evaporated on the steam-bath. The residue crystallised when rubbed with ether-ligroin. Crystallisation from ethyl acetate-ligroin (b. p. 60—80°) gave *2-keto-3-methyltetrahydrofuran-5-acetic-5-carboxylic acid* (X), m. p. 186° (Found: C, 47·8; H, 5·1.  $C_8H_{10}O_6$  requires C, 47·5; H, 4·95%).

*Ozonolysis of the Ester (I).*—The solution resulting from the passage of ozonised oxygen through a solution of approximately 1 g. of the ester in chloroform at 0° for 24 hours was evaporated in a vacuum at room temperature, and the syrupy residue decomposed by shaking with cold water for 48 hours. A small amount of crystalline material, m. p. approx. 115°, remained undissolved, but was converted into a gum when crystallisation from dilute alcohol was attempted. Distillation of a portion of the aqueous solution gave some formaldehyde, identified as its dimedon compound, m. p. and mixed m. p. 189—190°. The presence of oxalic acid was demonstrated in the usual manner in the residual aqueous liquor. No crystalline or identifiable products were obtained from the ethereal extract of the aqueous liquor.

*Ozonolysis of the Acid (IV).*—Similar ozonolysis of this acid gave an insoluble, partly crystalline ozonide which was decomposed by boiling with water. The volatile products, passed into a solution of *p*-nitrophenylhydrazone in dilute hydrochloric acid, gave a small amount of a reddish precipitate, decomp. 260—265°. Formaldehyde was also detected as its dimedon compound in the aqueous distillate. The residual aqueous liquor was oxidised with sodium bicarbonate and perhydrol at room temperature for several days, and the neutral and acid fractions isolated with ether in the usual manner. The former gave only a trace of crystalline material too small for investigation, whilst the acid residue had the strong odour of formic acid and reduced

ammoniacal silver nitrate and acid permanganate. The aqueous acidified mother-liquor was evaporated to dryness on a steam-bath, and the residue repeatedly extracted with dry acetone. The residue from the evaporated extract was unsaturated towards Baeyer's reagent and, after crystallisation from ether-ligroin, had m. p.  $118^{\circ}$ , depressed to  $105^{\circ}$  by the original acid (IV), and to  $100\text{--}104^{\circ}$  by admixture with methylsuccinic acid. The mixture with *dl*-malic acid, m. p.  $134^{\circ}$ , softened at  $128^{\circ}$  and had m. p.  $134^{\circ}$  (Found, in sample dried at room temp. in a vacuum: C, 35.0; H, 4.3. Calc. for  $C_4H_6O_5$ : C, 35.8; H, 4.5%).

*Synthesis of  $\alpha$ -Methylmuconic Acid.*— $\alpha$ -Methyladipic acid (1.2 g. prepared by alkaline hydrolysis of ethyl 2-methylcyclopentanone-2-carboxylate) and 6.5 g. of phosphorus pentabromide were warmed together on a steam-bath until the action was complete; 2.4 g. of dry bromine were added, and the mixture was heated on the steam-bath in the direct light of a 100-watt lamp for 18 hours. The product was refluxed with ligroin at  $40\text{--}60^{\circ}$ , evaporated, and, when cold, was poured dropwise into a solution of 20 g. of potassium hydroxide in 40 c.c. of 96% alcohol at  $0^{\circ}$ . The alkaline solution was gently refluxed for one hour, cooled to  $0^{\circ}$ , and non-acidic material extracted with ether. The aqueous liquor was added to ice-cold concentrated hydrochloric acid, extracted with ether, and the dried ethereal solution concentrated to small bulk.  *$\alpha$ -Methylmuconic acid*, m. p.  $276^{\circ}$  (decomp.), separated (Found: C, 54.1; H, 5.2.  $C_7H_8O_4$  requires C, 53.9; H, 5.1%). This acid was highly unsaturated and was rapidly reduced by hydrogen and platinum-black in aqueous alcohol. Isolation of the product in the usual manner gave  $\alpha$ -methyladipic acid, m. p. and mixed m. p.  $59^{\circ}$ .

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