702. 1 : 2-*Dicarboxylic Acids. Part I. Positional Isomerides Derived from Methylsuccinic Acid; with a Note on the Rearrangement of Unsymmetrical Compounds of this Type.*

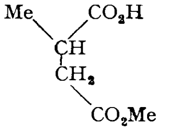
By J. E. H. Hancock and R. P. Linstead.

The two positionally isomeric half methyl esters (I and II) of methylsuccinic acid have been obtained in a pure crystalline state for the first time. Isomeride (I) was best prepared by hydrogenation of the corresponding half-ester of itaconic acid (IV); isomeride (II) was isolated by low-temperature crystallisation of the mixture obtained by esterification of methylsuccinic anhydride. These half-esters have been converted into the corresponding anilic esters which have been linked with the two anilic acids obtained from methylsuccinic anil. The structures of the various isomerides have been established and the work connected with that of previous investigators. Alkaline hydrolysis of the two anilic esters gives the same mixture of anilic acids and appears to proceed abnormally through intermediate formation of the anil. Electrolysis of the mixed half-esters gave a mixture of dimethyladipic esters from which *meso*-αα′-dimethyladipic acid was prepared.

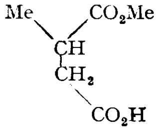
This series of papers will be largely concerned with derivatives of acids of the succinic and maleic series. Apart from their intrinsic interest, for example their ring closure to heterocyclic compounds and their rearrangements, they are of particular value as intermediates for the synthesis of conjugated macrocycles.

The two half-esters of methylsuccinic acid were recently required as intermediates in anodic syntheses. There was no definite evidence in the literature that either had ever been obtained pure, and a similar obscurity surrounded some other related unsymmetrical derivatives. As this is the simplest acid which can provide positionally isomeric derivatives of the types exemplified by the half-esters (I) and (II), it was desirable to determine whether two such series of compounds could be prepared in a homogeneous state and with known structure. This has now been done.

(I)



$\mathrm{Me{-}CH(CO_2H){-}CH_2{-}CO_2Me}$



$\mathrm{Me{-}CH(CO_2Me){-}CH_2{-}CO_2H}$

(II)

Previous preparations of the half-esters of methylsuccinic acid had yielded oily products, alike from the partial hydrolysis of diesters, partial esterification of the acid, and reaction of the anhydride with alcohols (Brühl and Braunschweig, *Ber.*, 1993, **26**, 337; Bone, Sudborough, and Sprankling, *J.*, 1904, **85**, 534). Half-esters prepared by these different methods had very similar physical properties, and, in the light of evidence presented later, there is no doubt that they were mixtures of positional isomers of types (I) and (II). A recent patent (U.S.P. 2,444,735) described the preparation of a half methyl ester by the interaction of methyl pyruvate and keten, followed by reduction of an intermediate β-lactone. Although this product was claimed to be the individual isomeride (II), it also was a liquid.

Our first experiments were on two processes which seemed likely to yield a homogeneous compound. In itaconic acid (III) the two carboxyl groups are attached to an unsaturated and a saturated carbon atom, respectively. This makes a well-established and decisive difference in their ease of esterification, and partial esterification following Anschütz and Drugman (*Ber.*, 1897, **30**, 2649, 2652) gave a homogeneous monomethyl ester to which the structure (IV) can be given with confidence. Catalytic hydrogenation of this gave a single methyl hydrogen methylsuccinate of m. p. 23—24°, which is assigned the methyl β-carboxybutyrate structure (I).*

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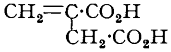
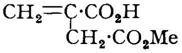
* Since the completion of the present work, B. R. Baker, Schaub, and Williams (*J. Org. Chem.*, 1952, **17**, 116) have described the preparation of a methyl hydrogen methylsuccinate by the same route and have proved it to have the structure (I) by an independent method. Their material was obtained as an oil but there can be no doubt that it was substantially identical with ours. Other points raised by the work of Baker *et al.* are dealt with later.

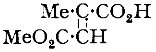
The same acid ester (I; m. p. 23—24°) was formed by the catalytic hydrogenation of the methyl hydrogen mesaconate, m. p. 50°, prepared following Anschütz by the partial hydrolysis of methyl mesaconate. To this half-ester Anschütz (*Annalen*, 1907, **353**, 139) had given the structure (V). This is in keeping with its non-identity with the position


$\begin{array}{l}CH_2{=}C{\cdot}CO_2H\\ \quad\ CH_2{\cdot}CO_2H\end{array}$

(III)


$\begin{array}{l}CH_2{=}C{\cdot}CO_2H\\ \quad\ CH_2{\cdot}CO_2Me\end{array}$

(IV)


$\begin{array}{r}Me{\cdot}C{\cdot}CO_2H\\ \| \quad\ \ \\ MeO_2C{\cdot}CH\quad\ \ \end{array}$

(V)

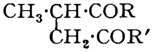
isomer prepared by Cloez (*Bull. Soc. chim.*, 1890, **3**, 598), and with Cocker and Fateen's recent proof of the structure of the ethyl hydrogen mesaconate prepared in a similar way (*J.*, 1951, 2630). The assignment of structure (I) to the half-ester of m. p. 23—24° agrees with these results.

The formation of half methyl esters from methylsuccinic anhydride was next examined. The product was a liquid mixture of isomers. When kept at low temperature it deposited a solid which after crystallisation from ether–light petroleum at —70° gave prisms of a second methyl hydrogen methylsuccinate, m. p. 42—43°. The same compound was obtained by partial esterification of methylsuccinic acid. The considerable practical difficulties in the isolation of this solid are described in the experimental section.

It was necessary to establish that the new solid was a definite position isomer and not a crystalline modification of the half-ester of m. p. 24°. For this purpose the two half-esters were converted into the ester anilides which were independently prepared from the anilic acid. Morrell (*J.*, 1914, **105**, 2698) had reported two anilic acids, m. p. 159° and 123°, and previous workers (Arppe and Biffi, *Annalen*, 1854, **90**, **141**; Anschütz, *ibid.*, 1888, **246**, 122; **248**, 273; Bone and Sprankling, *J.*, 1899, **75**, 859) had obtained one isomer, m. p. 148° (Anschütz, 143°). In our experiments the anil of methylsuccinic acid was hydrolysed with alkali, and the anilic acids liberated by fractional acidification and purified by crystallisation. Two isomeric anilic acids were obtained, one homogeneous of m. p. 149—150° and one of m. p. 118°, which subsequent work showed to be the nearly pure second form. The higher-melting isomer appears to exist in two crystalline modifications as is shown by Cocker and Fateen's work (*loc. cit.*). Treatment of the two anilic acids with diazomethane gave the corresponding anilic esters; the acid of m. p. 149° giving a homogeneous ester, m. p. 80°, and the acid of m. p. 118° a slightly impure ester which on crystallisation readily gave a pure compound, m. p. 85°. The m. p.–composition curve of the two isomeric anilic esters showed a considerable depression, there being a single eutectic, m. p. 55°, containing 52% of the isomeride of m. p. 80° [methyl α-(phenylcarbamylmethyl)-propionate (VI; R = OMe, R′ = NHPh)].

The two half methyl esters, m. p.s 24° and 43°, were linked to these two anilic esters through the ester chlorides. It has recently been established that the preparation of ester chlorides from unsymmetrical half-esters of the succinic, glutaric, or phthalic series may involve rearrangement (Cason, *J. Amer. Chem. Soc.*, 1947, **69**, 1548, etc.; Salmon-Legagneur and Soudan, *Compt. rend.*, 1944, **218**, 681; Ställberg-Stenhagen, *J. Amer. Chem. Soc.*, 1947, **69**, 2568; Chase and Hey, *J.*, 1952, 553), but Ställberg-Stenhagen has shown that this can be avoided by the use of oxalyl chloride under mild conditions. Using the same precautions, we converted the half-ester of m. p. 43° into the anilic ester of m. p. 80° and the half-ester of m. p. 24° into the anilic ester of m. p. 85°. In this way the existence of two distinct isomeric series was confirmed and the structure of the various compounds established (see the Table).

Positional isomerides of methylsuccinic acid (VI).


$\begin{array}{l}CH_3{\cdot}CH{\cdot}COR\\ \quad\ \ CH_2{\cdot}COR'\end{array}$

(VI)

R	OH	NHPh	NHPh	NMePh	NMePh	OMe	OMe	OH
R′	OMe	OMe	OH	OMe	OH	OH	NHPh	NHPh
M. p.	24°	85°	118° *	101°	149°	43°	80°	149°

* Not quite homogeneous.

The two isomeric anilic esters did not hydrolyse normally with cold aqueous alkali. Each gave a gum which subsequently solidified and then passed into solution; subsequent acidification gave a *mixture* of anilic acids. From the mixture derived from the anilic ester of m. p. 85°, the anilic acid of m. p. 149°, belonging to the other series, was isolated.

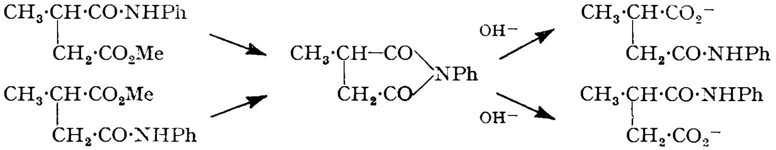
The *N*-methylanilic ester (VI; R = NMePh, R′ = OMe), m. p. 101°, was made from the half-ester of m. p. 24° through the ester chloride in the usual way. On hydrolysis with alkali it gave a homogeneous *N*-methylanilic acid which regenerated the original *N*-methylanilic ester, m. p. 101°, with diazomethane. The isomeric *N*-methylanilic ester derived from the half-ester of m. p. 43° was not obtained crystalline.

Further reference can now be made to the work of Baker, Schaub, and Williams (*loc. cit.*). From the (liquid) half-ester (I) by the same method they also obtained the *N*-methylanilic ester (VI; R = NMePh, R′ = OMe) of m. p. 100—101°, clearly identical with ours. By hydrolysis of this with hot alkali they obtained the corresponding acid (VI; R = NMePh, R′ = OH) which melted at 161—161·5° when pure. Our *N*-methylanilic acid melted at 149°. It seems probable that this discrepancy is due to dimorphism which is also encountered with the anilic acid (VI; R = OH, R′ = NHPh). The alternative explanation that our material contained some rearranged product seems unlikely because (*a*) our method of hydrolysis was milder than that used by Baker *et al.*, and (*b*) our acid regenerated the parent methyl ester with diazomethane. The second *N*-methylanilic acid (VI; R = OH, R′ = NMePh) has been prepared by Baker *et al.*; it melts at 77—78°. The American workers made the interesting observation that this material was rearranged to the high-melting isomer (at least partially) at 100°.

The Rearrangement of Unsymmetrical Derivatives of Succinic and Similar Acids.

It seems appropriate to make some comments on the mechanism of rearrangement of these unsymmetrical derivatives. These will be restricted to three examples: (i) our rearrangement of the anilic esters of methylsuccinic acid on alkaline hydrolysis; (ii) the thermal rearrangement of the *N*-methylanilide of methylsuccinic acid observed by Baker *et al.*; and (iii) the well-known rearrangement of the acid chlorides of half esters, recently reviewed in some detail by Chase and Hey (*loc. cit.*).

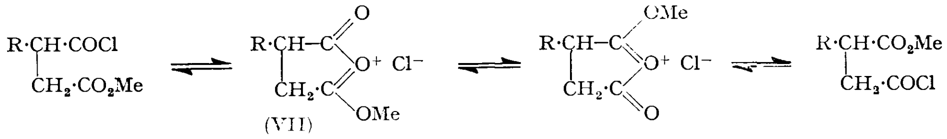
For reaction (i) the most probable mechanism is a preliminary elimination of methanol with the formation of the anil, followed by the fission of this by hydroxide ion, which is known to occur in both directions giving the two anilic acid ions:



This is supported by the absence of rearrangement in the hydrolysis of the *N*-methylanilic ester which cannot form the anil.

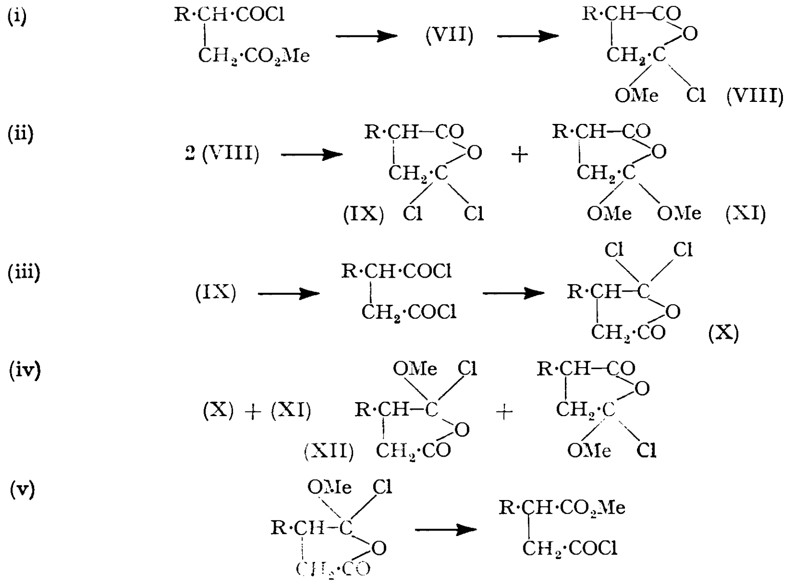
Reaction (ii) reasonably goes through anhydride which is subsequently split by methylaniline in both directions.

For reaction (iii) Chase and Hey mention as alternative intermediates the anhydride, an oxonium salt (VII), or an alkoxychlorolactone (VIII). It is debatable however, whether the last two are in fact alternatives. It seems plausible that the oxonium salt might well function as an intermediate in the formation of the lactone and that they are different stages in the same process. The crucial stage of the rearrangement is, however, the migration of the alkyl residue. One possibility is that this occurs in the cation of the oxonium salt:



(VII)

This bears a resemblance to trans-esterification but involves an *O*-alkyl fission. A further possibility which does not appear to have previously been considered is that the alkoxychlorolactone (VIII) disproportionates. The cyclic dichloride so formed (IX) undergoes a migration of chlorine; the new dichloride (X) then combines with a dimethoxy-compound (for example XI) by the reverse of the disproportionation; the isomeric alkoxychlorolactone (XII) is formed and this can tautomerise to the open-chain ester chloride with a structure isomeric with that of the starting material. The dimethoxy-compound involved in the reverse of the disproportionation can presumably have the open-chain or either of the two cyclic structures. The essential feature of this proposal is that it is a chlorine and not an alkoxy-group which migrates in the crucial stage.



It is possible to write a similar reaction scheme involving disproportionation of open-chain compounds but it would seem that the rearrangements are particularly easy among derivatives of acids which form heterocycles readily and reversibly : hence it is probable that the latter intervene, as has been generally thought.

The rearrangement may not necessarily involve the preformed half-ester half-chloride. It may occur during the reaction of the acid ester with the attacking reagent, such as thionyl chloride. Various special mechanisms involving the reagent then become possible.

Electrolyses. Preliminary experiments were carried out on the anodic coupling of the mixture of acid esters obtained by the action of methanol on methylsuccinic anhydride. This is rich in the isomer (II) of m. p. 43°. It was to be expected that in any case normal coupling of the Kolbe type would largely, if not exclusively, occur with this form and would be inhibited in the positional isomer because of the methyl group α- to carboxyl. Anodic coupling was carried out in methanol, by use of Linstead and Weedon's general technique (*J.*, 1950, 3326, etc). It gave a dimethyladipic ester fraction which on hydrolysis yielded some *meso*-αα'-dimethyladipic acid. This corresponds with the expected Kolbe coupling of the acid ester of m. p. 43°.

EXPERIMENTAL

Methylsuccinic anhydride was best prepared from the acid (*Org. Synth.*, **26**, 54) by Berner and Leonardsen's method (*Annalen*, 1939, **538**, 1). The yield of material, m. p. 33°, was 87%. Citraconic anhydride was hydrogenated extremely slowly over palladised barium sulphate in acetic acid or over Raney nickel in dioxan at 100°/100 atm.; this gave a 23% yield of the anhydride, m. p. 33°.

Methyl Hydrogen Methylsuccinate, m. p. 24° (*Methyl β-Carboxybutyrate*) (I).—(*a*) Methyl hydrogen itaconate (IV; Anschütz and Drugman, *loc. cit.*) formed long needles, m. p. 70° (lit., 67°) after repeated crystallisation from chloroform–light petroleum (Found : C, 50·3;

H, 5·8. Calc. for $C_6H_8O_4$: C, 50·0; H, 5·6%). It could also be purified, although slowly, by sublimation (Found: C, 49·9; H, 5·6%). Material prepared from itaconic anhydride and methanol was less easily obtained pure (m. p. 67—71°).

Methyl hydrogen itaconate (13·3 g.) in methanol (130 c.c.) was hydrogenated over Adams's catalyst (0·94 g.). The oily product, freed from catalyst and solvent, was seeded and set aside for several days in a vacuum desiccator at 0°. The crystallised material was filtered off at 0°, pressed on a pre-cooled porous tile, and finally recrystallised from ether–light petroleum at −80°. This gave crystals (4·63 g.), m. p. 15—22°, yielding after 3 similar recrystallisations, pure methyl β-carboxybutyrate (I), m. p. 23—24·2°. The oily filtrate, which contained unsaturated material, yielded more of the same product after rehydrogenation under 5 atmospheres pressure. The m. p. of the ester of m. p. 24° was somewhat depressed after distillation at 90°/0·8 mm. (bath-temp.).

(*b*) Dimethyl mesaconate was made by esterification following Stosius and Phillips's method (*Monatsh.*, 1924, **45**, 467). A solution of potassium hydroxide (8·9 g.) in methanol (150 c.c.) at 0° was treated slowly with dimethyl mesaconate (25 g.) in methanol (70 c.c.). After 52·5 hr., the product was separated by conventional procedures into acid and neutral fractions. The acid fraction after distillation at 149—157°/21 mm. (14·8 g.; 76%, with allowance for recovered diester) solidified to a mass of needles, m. p. 40—48°. Repeated crystallisation from petroleum gave a constant m. p. of 48—50·5°, unchanged by regeneration from the sodium salt. This pure methyl hydrogen mesaconate (V) (8·1 g.) was hydrogenated over Adams's catalyst in dry methyl acetate, first at atmospheric pressure and finally, after the addition of fresh catalyst, at 5 atm. The oily product was left to crystallise at 0° for several days in the presence of a seed of the half-ester of m. p. 24°. Seven crystallisations of the solid product from ether–petroleum gave pure methyl β-carboxybutyrate (I), m. p. 23—24°.

Methyl Hydrogen Methylsuccinate, m. p. 43° (*β-Carbomethoxybutyric Acid*) (II).—Methylsuccinic anhydride (32·2 g.) was heated under reflux with anhydrous methanol (11·5 c.c.) for 35 min. Next morning the product was distilled, 33·1 g. (80%) distilling at 93·5—94·7°/0·5 mm., n_D^{24} 1·4307. This material deposited much solid when kept at 0° for several days but the product very easily liquefied and gave only a few crystals when filtered through pre-cooled apparatus at 0°. It was accordingly dissolved in ether–light petroleum, and the temperature slowly lowered to −70°, a slight turbidity being maintained. The crystals which separated were filtered off at −80°, pressed on pre-cooled porous tile, and kept in a vacuum desiccator for several days at 0°. 1·53 g. of material melting at about 36—42° were obtained. Three repetitions of this process gave prisms of the pure β-carbomethoxybutyric acid (II), m. p. 42·5—43·5°. The analytical sample was dried at room temp. and 10^{-5} mm. (Found: C, 49·4; H, 7·1. $C_6H_{10}O_4$ requires C, 49·3; H, 6·9%) The *half-ester* was nearly unchanged after sublimation at 70°/10^{-2} mm. (bath temp.) (m. p. 41·5—43·5°).

Partial esterification of methylsuccinic acid with methanol (Fischer–Speier conditions; room temperature) gave, in addition to dimethyl ester, an acid ester fraction which failed to solidify when seeded with the half-ester of m. p. 24°. By the techniques described above, material, m. p. 38—41°, was obtained which was substantially the same as that made from the anhydride. Partial hydrolysis of the dimethyl ester with cold methanolic potash yielded an acid ester fraction in 65% yield, having b. p. 85·5°/0·3 mm., n_D^{24} 1·4305 (Found: equiv., 145·9. Calc., 146·1). This partially crystallised when seeded at 0° with the half-ester of m. p. 43° but not with the isomeride, m. p. 24°.

Anilic Acids and Esters from Methylsuccinic Anil.—The anil was prepared from the acid and aniline by Morrell's method (*loc. cit.*). The yield of the distilled product was 96%; the m. p. after three crystallisations from water was 105°. The anil sublimed slowly at 100° under atmospheric pressure.

The anil (7·1 g.) was treated for 30 min. with 2N-sodium hydroxide (22·5 c.c.). The clear solution was acidified with 2N-hydrochloric acid, added dropwise with mechanical stirring. Solid was collected at intervals, washed with water, dried (NaOH) at 0·1 mm., and weighed. In this way a total yield of 95% of anilic acid was obtained. The first crop (about 50%) melted at 143—145° and after two crystallisations from ethyl acetate gave α-(phenylcarbamylmethyl)-propionic acid (VI; R = OH, R′ = NHPh), m. p. 148·5—150·5°. After seven further crops of mixed anilic acids had separated, the residual solution was acidified with concentrated hydrochloric acid and cooled in ice–salt. The final product so precipitated (120 mg.; m. p. 111—112·5°) had m. p. 117·5—118° after three crystallisations from chloroform and was almost pure β-phenylcarbamylbutyric acid (VI; R = NHPh, R′ = OH).

The two anilic acids were esterified with ethereal diazomethane. The isomeride of m. p.

149° gave *methyl* α-(*phenylcarbamylmethyl*)*propionate* (VI; R = OMe, R′ = NHPh), m. p. 79·4—80° (from petroleum containing a little benzene) (Found: C, 65·2; H, 7·0; N, 6·3. $C_{12}H_{15}O_3N$ requires C, 65·1; H, 6·8; N, 6·3%). The ester from the anilic acid of m. p. 118°, twice crystallised from petroleum, melted at 82·5—84°. A mixture with the anilic ester, m. p. 85°, prepared as described below, melted at 84°. The substance was therefore nearly pure methyl β-phenylcarbamylbutyrate (VI; R = NHPh, R′ = OMe).

Anilic Esters from Acid Esters of Methylsuccinic Acid.—Methyl β-carboxybutyrate (I; m. p. 24°; 655 mg., from methyl hydrogen mesaconate) in dry benzene (1 g.) and oxalyl chloride (657 mg.) were warmed at 30—40° for 3 hr., and the solvent evaporated at 40°/12 mm. The product was taken up in dry benzene and again evaporated, and this operation was repeated twice. The residue was dissolved in dry ether (4 c.c.) and carefully treated at 0° with aniline (1·2 c.c.) in the same solvent. The neutral product, isolated in the usual manner (782 mg., 79%), was pure *methyl* β-*phenylcarbamylbutyrate* (VI; R = NHPh, R′ = OMe), m. p. 84—85°. A similar preparation from methyl β-carboxybutyrate, m. p. 24° [prepared from methyl hydrogen itaconate (IV)] and three crystallisations of the anilic ester from petroleum yielded fine needles, m. p. 84—85° (Found: C, 65·2; H, 7·0; N, 6·55. $C_{12}H_{15}O_3N$ requires C, 65·1; H, 6·8; N, 6·3%). The correct values for carbon and hydrogen were obtained only by combustion of the compound mixed with potassium dichromate. There was no depression in melting point when the two preparations described above were mixed.

The isomeric half-ester (II), m. p. 43°, was similarly treated with oxalyl chloride, followed by aniline. The product (81%) was methyl α-(phenylcarbamylmethyl)propionate (VI; R = OMe, R′ = NHPh), m. p. 79—80·5° not depressed on admixture with a sample prepared by esterification of the anilic acid, m. p. 149°, but greatly depressed by the isomeric anilic ester, m. p. 85°.

A melting point–composition curve was determined for mixtures of the two anilic esters. Such mixtures began to soften at 50—60°; the temperatures given below are those when a homogeneous liquid was formed:

% of (VI; R = OMe, R′ = NHPh) ...	0	10	21	32	40	50	59	70	79	90	100
M. p., ° c	85	82	78·5	72	64	57	61·5	68	73	78	80

The eutectic contains 52% of (VI; R = OMe, R′ = NHPh) and is at 54·5°.

Mixtures of the isomeric half methyl esters of methylsuccinic acid could be roughly analysed by conversion through the ester chloride into the anilic ester, followed by determination of m. p. and mixed m. p.s. The mixed anilic ester first separated as a gum which was difficult to manipulate; and this lessened the quantitative significance of the results. The indications were that the mixed half-ester obtained by esterifying methylsuccinic anhydride contained about two-thirds of the isomeride (I); while in that from partial hydrolysis of the diester the compound (II) preponderated.

Alkaline Hydrolysis of Anilic Esters.—Methyl β-phenylcarbamylbutyrate (VI; R = NHPh, R′ = OMe) (157 mg.), m. p. 85°, was treated with N-potassium hydroxide (1 c.c.); a gum separated which rapidly solidified. On the addition of alcohol (5 c.c.), the mixture became homogeneous. After 12 days at room temperature the solvent was removed in a vacuum-desiccator, the gum was dissolved in a little water, and the product acidified with N-hydrochloric acid (2·5 c.c.). After a night at 0° the precipitated anilic acid was filtered off and washed with water at 0°. The undissolved portion (98 mg., 67%) melted at 134—137°; the filtrate slowly deposited a solid, m. p. 117—120° (20 mg., 14%). The solid of m. p. 134—137° after four crystallisations from ethyl acetate melted at 147—148° and at 148—148·5° in admixture with the anilic acid of m. p. 149° (VI; R = OH, R′ = NHPh). The low-melting fractions were mixtures from which the isomeric anilic acid (VI; R = NHPh, R′ = OH), m. p. 117·5—118°, was obtained nearly pure by crystallisation from chloroform (Found: C, 63·0; H, 6·3. Calc. for $C_{11}H_{13}O_3N$: C, 63·75; H, 6·3%).

Methyl α-(phenylcarbamylmethyl)propionate (VI; R = OMe, R′ = NHPh), m. p. 80°, was hydrolysed similarly. It gave in 74% yield a similar mixture, m. p. 129—136°, of anilic acids. The pure anilic acid, m. p. 149°, was quite unaffected by treatment with alkali under the conditions of hydrolysis.

Methyl β-carboxybutyrate (I; m. p. 24°) was converted into the corresponding *N*-methyl-anilic ester by successive treatments with oxalyl chloride and *N*-methylaniline, following the procedure given above for the corresponding anilide. The reaction product melted at 97—100·5° and gave the homogeneous *methyl* β-N-*methylphenylcarbamylbutyrate* (VI; R = NMePh, R′ = OMe), m. p. 100·5—101°, constant after one crystallisation from ethyl acetate–petroleum (Found: C, 67·3; H, 7·4; N, 6·0. $C_{13}H_{17}O_3N$ requires C, 66·4; H, 7·3; N, 6·0%).

The *N*-methylanilic ester was hydrolysed with alkali by the method described for the anilic esters. The crude acid, isolated in almost quantitative yield, after one crystallisation from ethyl acetate gave β-N-*methylphenylcarbamylbutyric acid* (VI; R = NMePh, R′ = OH), as prisms, m. p. 148·5—149·5° (Found : C, 65·8; H, 7·0; N, 7·1. $C_{12}H_{15}O_3N$ requires C, 65·1; H, 6·8; N, 6·3%). Esterification with diazomethane re-formed the original *N*-methylanilic ester; m. p. 99—100° (crude), 99—100·5° after one crystallisation, mixed m. p. the same.

Electrolysis of Mixed Half-esters of Methylsuccinic Acid.—The general technique described by Linstead and Weedon (*loc. cit.*) was followed. The mixed half-ester, obtained by esterifying methylsuccinic anhydride (10·7 g.), in anhydrous methanol (25 c.c.) containing 0·02 equiv. of sodium was electrolysed by a current of 1·5 A at 110 V between smooth platinum electrodes. After 107 min. the mixture became alkaline, this corresponding to a 36% excess of current over the theoretical. The product was acidified with a few drops of acetic acid and freed from solvent. On distillation 2·24 g. of a neutral oil were obtained, b. p. 112—116°/13 mm., $n_D^{22.5}$ 1·4295; corresponding to a 30% yield of dimethyladipic ester. This fraction was hydrolysed with boiling hydrochloric acid (1 : 1). The product was a gum which after some months deposited a solid; this was triturated with benzene and filtered off; it had m. p. 128—139°. The yield of gummy acid was nearly theoretical but that of solid was only 7%. After three crystallisations from hydrochloric acid (1 : 1) the solid gave prisms of *meso*-αα′-dimethyladipic acid, m. p. 141—142° alone or in admixture with an authentic specimen (Noyes and Kyriakides, *J. Amer. Chem. Soc.*, 1910, **32**, 1057).

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