

## Studies on Succinic Acids

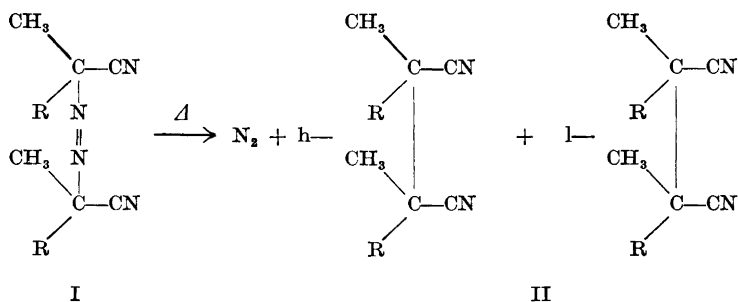
### V. The Preparation and Properties of Diastereoisomers of Tetraalkylsuccinic Acids

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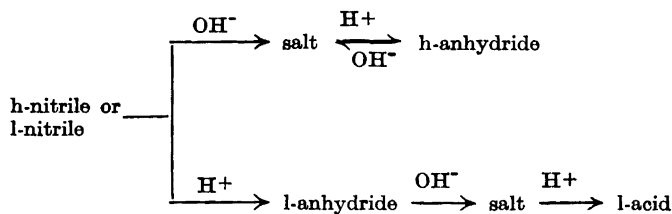
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The diastereoisomers of three tetraalkylsuccinic acids containing two asymmetric centres, *viz.*  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -diethyl-,  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -dipropyl-, and  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -diisopropylsuccinic acid, have been prepared. Their relative configuration is discussed on the basis of dissociation constant measurements, and in each pair the isomer with lower ratio between  $K_1$  and  $K_2$  is proposed to be the *meso* form.

Only a few tetraalkylsuccinic acids containing two asymmetric centres have been described in the literature<sup>1-3</sup>. Stefl<sup>1</sup> prepared  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -diethyl- and  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -dipropylsuccinonitrile (II, R = C<sub>2</sub>H<sub>5</sub> and *n*-C<sub>3</sub>H<sub>7</sub>) by thermal decomposition of the corresponding bisazonitriles (I) and was able to isolate the diastereoisomers in a pure or almost pure state.



(The letters h and l designate high- and low-melting, respectively). He studied the hydrolysis of these dinitriles and summarized the results in the following scheme:



*i.e.* on hydrolysis both dinitriles were converted into the same anhydride, in alkaline medium into the high-melting anhydride and in acid medium into the low-melting anhydride. Furthermore, he also concluded that the h-anhydride was isomerised to the l-anhydride by treatment with concentrated hydrochloric acid at 180° for 6 h or with acetic anhydride at the boiling temperature for 12 h, whereas the inverse reaction was claimed to occur on boiling the l-anhydride with 40 % aqueous potassium hydroxide for 2–3 days\*.

Dox<sup>3</sup> synthesised  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -diethylsuccinic acid by the bisazonitrile method and converted it into the anhydride and the imide but did not attempt to separate it into diastereoisomers.

The present author<sup>2</sup> has prepared  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -diethylsuccinic acid and  $\alpha,\alpha'$ -diethyl- $\alpha,\alpha'$ -diisopropylsuccinic acid by Kolbe electrolysis of the appropriate malonic monoesters, but could not separate them into diastereoisomers by fractional crystallisation. In the latter case the ease of formation of the anhydride from the acid both in solution and in the solid state made this procedure impossible.

It is now of course apparent that the isomerisations described by Stefl are not consistent with modern theories on the mechanism of inversion at an asymmetric carbon atom, since there is no mechanism for inversion at a quaternary carbon atom which does not involve scission and recombination of a carbon to carbon bond and this possibility seems very unlikely in view of the rather mild reaction conditions that Stefl used. Another point worthy of note is the failure to isolate the h-acid, the solution of the h-acid salt giving the h-anhydride directly on acidification. Tetraalkylsuccinic acids certainly have a very strong tendency to lose water forming anhydrides<sup>2,4,5</sup>, but both tetraethyl- and tetrapropylsuccinic acid are liberated as the free acids by acidification of solutions of their salts. It is evident that some of the results must have been misinterpreted. The present paper deals with the problem of preparing pure diastereoisomers of some  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -dialkylsuccinic acids and with evidence on the steric relationships between the acids obtained from dissociation constant measurements.

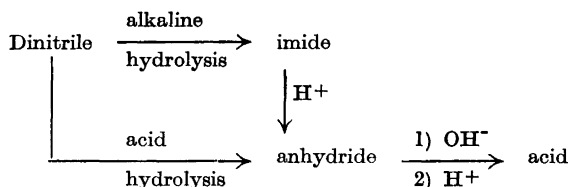
#### $\alpha,\alpha'$ -Dimethyl- $\alpha,\alpha'$ -diethylsuccinic acid

The product of hydrolysis of dimethyl  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -diethylsuccinate by concentrated sulphuric acid was a liquid anhydride with rapidly dissolved in boiling 10 % aqueous sodium hydroxide solution<sup>2</sup>. On acidification this

\* The present author was not able to duplicate the last-mentioned reaction with  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -diethylsuccinic acid prepared in a different way<sup>2</sup>.

gave a mixture of acids, m.p. 125–40°, which could not be separated by fractional crystallisation using several different solvents and solvent pairs. The acid slowly changes into the anhydride in solution, which complicates the separation procedure, since contamination by a small amount of anhydride considerably lowers the melting points of the acid. The melting point determinations must be done in sealed capillaries and the heating rate and time must be carefully controlled in order to obtain reproducible values<sup>2,6</sup>.

An attempt was then made to prepare the acids by the bisazonitrile method since this permits the separation of the two forms at the dinitrile stage<sup>1</sup>, and no inversion would be expected to occur during the hydrolysis. In fact the two nitriles were easily separated by fractional crystallisation from ligroin, and were then hydrolysed according to the following scheme:



In no case was any interconversion between the two diastereoisomeric series observed. The m.p.'s of the various compounds are listed in Table 1.

Table 1. Melting points of diastereoisomers of  $\alpha, \alpha'$ -dimethyl- $\alpha, \alpha'$ -diethylsuccinic acid and their derivatives

	Imide, m.p.	Anhydride, m.p.	Acid, m.p.
High-melting dinitrile, m.p. 99–101°	97–99°	32–33°	189–192°
Low-melting dinitrile, m.p. 44–45°	92–95°	40–42°	182–184°

The melting point differences between the two series are rather small for the imides, anhydrides and acids, and it is difficult to identify the diastereoisomers by melting point determinations only. In the light of these findings the results reported by Stefl are quite understandable. The "h-anhydride" must actually have been the h- and l-imide, which were mistaken for the same compound. These imides dissolve in aqueous sodium hydroxide and are precipitated by acidification, which explains why the "h-acid" was never obtained. The apparent transformation of "h-anhydride" into "l-anhydride" by concentrated hydrochloric acid was a hydrolysis of the imides to the anhydrides. The "l-anhydride" apparently was either the h- or l-anhydride (or, as the dinitriles were not always separated from each other, a mixture of the anhydrides) and similarly the "l-acid" was either h- or l-acid (or a mixture). The small differences in melting point and solubility are probably responsible for Stefl's misinterpretation, especially as he never obtained the anhydrides in the solid state and the care necessary in m.p. determinations on the acids was not fully known at that time.

*$\alpha,\alpha'$ -Dimethyl- $\alpha,\alpha'$ -dipropylsuccinic acid*

This acid was best prepared by Kolbe electrolysis of monoethyl methylpropylmalonate. The succinic ester was easily hydrolysed by treatment with warm concentrated sulphuric acid, giving a mixture of anhydrides. The acid mixture obtained by alkaline hydrolysis of the anhydride and acidification was separated into two forms by fractional crystallisation from ethyl acetate, m.p. 173–175° and 166–167°, respectively. The corresponding anhydrides were liquid. The bisazonitrile method was also used but was not superior to the Kolbe method as the over-all yield of the dinitriles was low and they were impossible to separate by fractional crystallisation. The high-melting isomer was obtained in a pure state but the other fractions obtained were always mixtures of varying composition. It was established however that the high-melting dinitrile corresponded to the high-melting acid. Steff's results with this acid can presumably be explained in the same way as for the  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -diethylsuccinic acid.

 *$\alpha,\alpha'$ -Dimethyl- $\alpha,\alpha'$ -diisopropylsuccinic acid*

This pair of acids was prepared by Kolbe electrolysis of monoethyl methylisopropylmalonate and subsequent treatment in the same way as for the *n*-propyl compound. The melting points of the acids were 175–177° (anhydride 65–66°) and 130–131° (anhydride 78–79°), respectively. Again the bisazonitrile method gave a low over-all yield of dinitriles, and only the high-melting compound was obtained pure, m.p. 67–68°. This isomer corresponded to the high-melting acid.

 *$\alpha,\alpha'$ -Dimethyl- $\alpha,\alpha'$ -di(*tert.*-butyl)-succinic acid*

The dimethyl ester of this acid has been prepared by Ansell *et al.*<sup>7</sup> It was not possible to hydrolyse the ester with concentrated sulphuric acid, and therefore the Kolbe method could not be used. The bisazonitrile method also failed because the intermediate radicals disproportionate instead of coupling. The reaction product on hydrolysis with strong sulphuric acid gave methyl-(*tert.*-butyl)-acetic acid in low yield.

## DISCUSSION

The dissociation constants of the three acid pairs were determined in 50 % (by wt). aqueous ethanol by potentiometric titration<sup>8</sup>. The  $pK_1$ ,  $pK_2$ , and  $\Delta pK$  values are given in Table 2. Corresponding values for  $\alpha,\alpha'$ -diethyl-,  $\alpha,\alpha'$ -diisopropyl-, tetramethyl-, and tetraethylsuccinic acid have been included for comparison.

The dissociation constants of a number of *meso* and *racemic*  $\alpha,\alpha'$ -dialkylsuccinic acids and tetraalkylsuccinic acids and the  $K_1/K_2$  ratios<sup>8,9</sup> for these compounds indicated that: Firstly, in an  $\alpha,\alpha'$ -dialkylsuccinic acid the alkyl

Table 2. Thermodynamic dissociation constants of alkylsubstituted succinic acids in 50 % (by wt.) aqueous ethanol

Succinic acid	$pK_1$	$pK_2$	$\Delta pK$
$\alpha,\alpha'$ -Dimethyl- $\alpha,\alpha'$ -diethyl-, m.p. 189–92° <sup>a</sup>	5.73	9.66	3.93
$\alpha,\alpha'$ -Dimethyl- $\alpha,\alpha'$ -diethyl-, m.p. 182–4° <sup>a</sup>	4.45	10.44	5.99
$\alpha,\alpha'$ -Dimethyl- $\alpha,\alpha'$ -dipropyl-, m.p. 173–5°	5.73	9.99	4.26
$\alpha,\alpha'$ -Dimethyl- $\alpha,\alpha'$ -dipropyl-, m.p. 166–7°	4.56	10.86	6.30
$\alpha,\alpha'$ -Dimethyl- $\alpha,\alpha'$ -diisopropyl-, m.p. 175–7°	6.92	9.32	2.40
$\alpha,\alpha'$ -Dimethyl- $\alpha,\alpha'$ -diisopropyl-, m.p. 130–1°	3.20	13.13	9.93
Racem- $\alpha,\alpha'$ -diethyl- <sup>b</sup>	4.76	9.22	4.46
Meso- $\alpha,\alpha'$ -diethyl- <sup>b</sup>	5.37	7.43	2.06
Racem- $\alpha,\alpha'$ -diisopropyl- <sup>b</sup>	3.66	11.44	7.78
Meso- $\alpha,\alpha'$ -diisopropyl- <sup>b</sup>	5.98	8.10	2.12
Tetramethyl- <sup>b</sup>	4.84	10.13	5.29
Tetraethyl- <sup>b</sup>	4.78	11.42	6.64

<sup>a</sup>  $\alpha,\alpha'$ -Dimethyl- $\alpha,\alpha'$ -diethylsuccinic acid prepared by the Kolbe method gave  $pK_1$  and  $pK_2$  values of 4.86 and 10.16 respectively<sup>b</sup>. Obviously this sample was a mixture of diastereoisomers.

groups have a tendency to take up positions *trans* to each other; in the *meso* acids this brings the carboxyl groups into a *trans* configuration and in the *racemic* acid into a *gauche* configuration. In the latter case a high  $K_1/K_2$ -ratio is obtained partly due to the formation of an internal hydrogen bond in the mono-anion, partly to increased Coulomb interaction between the carboxyl groups. Secondly, the accommodation of alkyl groups in, for instance, a tetraalkylsuccinic acid molecule introduces steric strain, which would be reduced in the cyclic hydrogen-bonded structure.

It is evident that these two factors cannot always be easily distinguished. In the tetraalkylsuccinic acids of the type studied in this paper the molecule is highly strained due to the presence of the four alkyl groups, and it can be expected that the two more bulky alkyl groups will have the greater influence on the conformational equilibrium. In the hydrogen-bonded structure, for the *meso* acid mono-anion the methyl groups will lie on one side of the ring and the more bulky groups on the other side. In the other possible *meso* acid conformation all groups will be *trans* staggered and this would be energetically favoured if there was no interaction between the carboxyl groups.

In the *racemic* acid mono-anion with a cyclic structure the bulky alkyl groups will be situated *trans* to each other and this arrangement will therefore be less strained than that of the corresponding *meso* form. From these considerations it can be concluded that the *meso* acid should possess a lower  $K_1/K_2$ -ratio than the *racemic* acid since: (1) in the fully *trans* staggered conformation the Coulomb interaction between the carboxyl groups is less than that of the most favoured *racemic* acid conformation (which has the carboxyl groups *gauche*) and moreover the formation of an internal hydrogen bond is not possible, and 2) if a cyclic *meso* acid conformation is present in appreciable amounts, it must nevertheless be less stable than the corresponding *racemic*

form. On these grounds the acids with the lower  $\Delta pK$  in Table 2 are ascribed the *meso* configuration. The m.p.'s and solubility relationships are in agreement with this.

#### EXPERIMENTAL

The analyses were done by the Department of Analytical Chemistry, Chemical Institute, University of Lund. Melting points were determined with a Kofler apparatus unless otherwise stated. M.p.'s in sealed capillaries (abbreviated s.c.) were done as described in paper II of this series.

#### *a,a'*-Dimethyl-*a,a'*-diethylsuccinic acid

A. *Bisazonitrile method.* Hydrazine sulphate (96 g) and sodium cyanide (75 g, 97–98 %) were dissolved in 1500 ml of water in a three litre bottle. Methyleneethyl ketone (96 g) was added and the mixture was shaken for 48 h. The organic layer was then taken up in ether, the ether was removed by evaporation *in vacuo* at room temperature and the residue, a viscous oil (120 g) which did not crystallise even after standing for several days in a vacuum desiccator, was dissolved in 200 ml of acetic acid + 100 ml of concentrated hydrochloric acid. The mixture was cooled to 5°, and an equimolecular amount of bromine dissolved in 400 ml of 70 % aqueous acetic acid was added with vigorous stirring during the course of 2 min. Stirring was continued for half an hour and the reaction mixture was then poured into ice water (3 l). The precipitate was collected, washed thoroughly with water, and dried giving the crude bisazonitrile (93 g), m.p. 49–51°, m.p. after recrystallisation from light petroleum 50–51° (80 g). Stefl<sup>1</sup> reported m.p. 54–55°, Dox<sup>3</sup> 57°, and Overberger *et al.*<sup>10</sup> 49–51°.

The recrystallised, dry bisazonitrile (80 g) was decomposed by boiling in carbon tetrachloride (500 ml) for 20 h. The solvent was distilled off and the residue was subjected to fractional crystallisation from ligroin. The more insoluble fraction (30 g) had m.p. 70–90°. One recrystallisation from ligroin afforded pure high-melting *a,a'*-dimethyl-*a,a'*-diethylsuccinonitrile (25 g, 22 %), m.p. 99–101°. The low-melting isomer was isolated from the mother liquor, m.p. 44–45° after two recrystallisations from ligroin; the yield of pure low-melting *a,a'*-dimethyl-*a,a'*-diethylsuccinonitrile was 19.5 g (17 %). Stefl<sup>1</sup> reported m.p. 98–99° and 42–43°, respectively. For the high-melting form Overberger *et al.*<sup>10</sup> found m.p. 96–98°.

The high-melting *a,a'*-dimethyl-*a,a'*-diethylsuccinonitrile, 10 g, was hydrolysed by boiling with a mixture of concentrated sulphuric acid (50 ml), water (20 ml) and acetic acid (60 ml) for 20 h. The reaction mixture was poured into water, the organic layer was taken up in ether, the ether solution was washed with sodium carbonate solution and water, and finally the ether was distilled off. The residue was distilled *in vacuo*, b.p. 117–118°/10 mm. The main fraction (9.2 g) solidified on standing, m.p. 30–33°, and was recrystallised from light petroleum, m.p. 32–33°. According to the analysis it was an anhydride of *a,a'*-dimethyl-*a,a'*-diethylsuccinic acid. (Found: C 65.2; H 8.9; Calc. for C<sub>10</sub>H<sub>16</sub>O<sub>3</sub>: C 65.2; H 8.8). The anhydride was dissolved in 10 % aqueous potassium hydroxide by boiling for 30 min. Addition of dilute hydrochloric acid precipitated the high-melting *a,a'*-dimethyl-*a,a'*-diethylsuccinic acid, which was crystallised from ethyl acetate, m.p. 189–192° (s.c.). (Found: C 59.5; H 9.2; equiv. wt 204. Calc. for C<sub>10</sub>H<sub>18</sub>O<sub>4</sub>: C 59.4; H 9.0; equiv. wt 202).

The high-melting *a,a'*-dimethyl-*a,a'*-diethylsuccinonitrile was hydrolysed under alkaline conditions by boiling with 30 % aqueous potassium hydroxide for 48 h. The reaction mixture was extracted with ether to remove any remaining nitrile, and the aqueous layer was acidified with dilute hydrochloric acid. The crystalline material deposited was collected and recrystallised from ligroin, m.p. 97–99°; according to analyses this material was *a,a'*-dimethyl-*a,a'*-diethylsuccinimide. (Found: C 65.5; H 9.3; N 7.7. Calc. for C<sub>10</sub>H<sub>17</sub>O<sub>2</sub>N: C 65.5; H 9.3; N 7.7). Dox<sup>3</sup> reported m.p. 93–4° for an imide of unspecified configuration. The imide was hydrolysed to the anhydride, m.p. 32–33°, by boiling for 8 h with concentrated sulphuric acid, water, and acetic acid in the same proportions as above.

Low-melting  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -diethylsuccinonitrile (10 g) was hydrolysed in the same way as for the high-melting nitrile. The  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -diethylsuccinic anhydride obtained (9.0 g), b.p. 124–126°/12 mm, m.p. 39–41°, was recrystallised from light petroleum, m.p. 40–42°. (Found: C 64.9; H 8.7. Calc. for  $C_{10}H_{16}O_3$ : C 65.2; H 8.7). Hydrolysis gave the low-melting  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -diethylsuccinic acid, m.p. 182–184° (s.c.) after recrystallisation from ethyl acetate. (Found: C 59.3; H 9.0; equiv. wt 203. Calc. for  $C_{10}H_{16}O_4$ : C 59.4; H 9.0; equiv. wt 202).

Alkaline hydrolysis of the low-melting dinitrile in the same way as for the high-melting nitrile afforded an  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -diethylsuccinimide of m.p. 92–95° after recrystallisation from ligroin. (Found: C 65.5; H 9.4; N 7.6. Calc. for  $C_{10}H_{17}O_2N$ : C 65.5; H 9.4; N 7.7). Acid hydrolysis of this imide gave the anhydride, m.p. 40–42°.

B. *Kolbe method.* A crude mixture of the two diastereoisomeric acids was prepared as described previously<sup>2</sup>. Fractional crystallisation was tried with ethyl acetate, benzene, ethyl acetate-benzene, and ethyl acetate-light petroleum, but no separation was achieved. The sample with highest m.p. melted at 173–176° (s.c.). The products isolated from the mother liquors were largely anhydrides.

### $\alpha,\alpha'$ -Dimethyl- $\alpha,\alpha'$ -dipropylsuccinic acid

A. *Bisazonitrile method.* The bishydrazonitrile was prepared in the same way as for the methylethyl derivative from hydrazine sulphate (96 g), sodium cyanide (75 g), and methyl propyl ketone (115 g) in water (1 500 ml). The crude product (125 g) was oxidised directly with bromine in aqueous acetic acid as described above. The crystalline product obtained was contaminated with a strongly lachrymatory oil, which was removed by suction on a sintered glass-funnel. The nature of this product was not investigated. The product was recrystallised from light petroleum, m.p. 55–70°, yield 42 g. Stefl<sup>1</sup> reported m.p. 64° and Overberger *et al.* 73–74.5°. The bisazonitrile was decomposed by boiling in carbon tetrachloride for 24 h. The solvent was distilled off, and the residue was distilled *in vacuo*, b.p. 106–110°/0.5 mm. The main fraction (27 g, 21 %) solidified on standing over night, m.p. 40–70°. In spite of several attempts to separate the two isomers by fractional crystallisation from various solvents, only the high-melting, less soluble form was obtained in a pure state, m.p. 83–85° after three recrystallisations from ligroin. Stefl reported m.p. 84° for the high-melting form and that the other isomer was liquid. Overberger *et al.*<sup>10</sup> gave m.p. 83–83.5° for the high-melting form.

The mixture of dinitriles (10 g) was hydrolysed with sulphuric acid – water – acetic acid and the crude anhydride was directly hydrolysed in the same way as before. The dried acid was dissolved in the minimum of ethyl acetate and the solution was treated with decolorising carbon, filtered, and allowed to cool. The crystals were filtered off, m.p. 171–175° (s.c.) and recrystallised from ethyl acetate, m.p. 173–175° (s.c.). According to analyses this substance was an  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -dipropylsuccinic acid. (Found: C 62.3; H 9.5; equiv. wt 228. Calc. for  $C_{12}H_{22}O_4$ : C 62.6; H 9.6; equiv. wt 230). The anhydride was prepared by treating the acid with excess acetyl chloride. Distillation gave the pure  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -dipropylsuccinic anhydride, b.p. 114–116°/12 mm. (Found: C 67.7; H 9.6. Calc. for  $C_{12}H_{20}O_3$ : C 67.9; H 9.5).

The mother liquor from the above filtration was diluted with five volumes of light petroleum giving a precipitate of the low-melting  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -diethylsuccinic acid, m.p. 158–162° (s.c.), which was recrystallised from acetic acid-ligroin (1:10), m.p. 166–167° (s.c.). (Found: C 62.4; H 9.4; equiv. wt 230. Calc. for  $C_{12}H_{22}O_4$ : C 62.6; H 9.6; equiv. wt 230). The anhydride was liquid, b.p. 115–118°/14 mm. (Found: C 67.9; H 9.5. Calc. for  $C_{12}H_{20}O_3$ : C 67.9; H 9.5). The amounts of pure acids isolated were 1.9 and 1.1 g, respectively, but the material could be recovered from the mother liquor as anhydride, for use in subsequent preparations.

The high-melting  $\alpha,\alpha'$ -dimethyl- $\alpha,\alpha'$ -dipropylsuccinonitrile was found to correspond to the high-melting acid.

B. *Kolbe method.* The preparation and electrolysis of monoethyl methylpropylmalonate was done in the same way as before<sup>2</sup>. The product was obtained in 35 % yield, b.p. 119–120°/2 mm,  $n_D^{20}$  1.4468,  $d_4^{20}$  0.9704. According to analyses it was the diethyl ester. (Found: C 66.7; H 10.5;  $\tau_D$  0.2752. Calc. for  $C_{16}H_{30}O_4$ : C 66.9; H 10.7;  $\tau_D$  0.2777). The

ester was hydrolysed with concentrated sulphuric acid in the usual way, and the acids were prepared as described for the anhydride obtained from the dinitriles. The pure acids melted at 174–175° (s.c.) and 166–167° (s.c.), respectively.

### *a,a'*-Dimethyl-*a,a'*-diisopropylsuccinic acid

**A. Bisazonitrile method.** The bishydrazoneitrile was prepared in the same way as the methylethyl derivative from hydrazine sulphate (96 g), sodium cyanide (75 g), and methyl isopropyl ketone (115 g) in water (1 500 ml). The crude product (125 g) was oxidised directly as described above. In this case also a strongly lachrymatory oil was formed that had to be removed by suction on a sintered glass-funnel. The crystalline mass was recrystallised from ethanol, m.p. 64–69°, yield 44 g. Overberger *et al.* found m.p. 68.5–70°. The bisazonitrile was boiled over night in carbon tetrachloride (250 ml). Distillation yielded a mixture of dinitriles, (16.5 g, 13 %), b.p. 142–145°/14 mm, which partially solidified after standing for a few days. Attempts to separate the two forms failed, and only the high-melting *a,a'*-dimethyl-*a,a'*-diisopropylsuccinonitrile could be obtained pure, m.p. 67–68° after recrystallisation from light petroleum. (Found: C 74.7; H 10.4; N 14.8. Calc. for C<sub>13</sub>H<sub>20</sub>N<sub>2</sub>: C 75.0; H 10.5; N 14.6).

The mixture of dinitriles (10 g) was hydrolysed as before. The anhydride obtained was purified by distillation, b.p. 110–111°/1.5 mm and this was converted to the acid in the usual way. The acid was dissolved in the minimum amount of boiling ethyl acetate as rapidly as possible. The high-melting *a,a'*-dimethyl-*a,a'*-diisopropylsuccinic acid which crystallised on cooling, was recrystallised from ethyl acetate, m.p. 169–172° (s.c.). (Found: C 62.4; H 9.6; equiv. wt 116. Calc. for C<sub>13</sub>H<sub>22</sub>O<sub>4</sub>: C 62.6; H 9.6; equiv. wt 115). The anhydride was prepared and recrystallised from light petroleum, m.p. 65–66° (Found: C 67.7; H 9.5; Calc. for C<sub>13</sub>H<sub>20</sub>O<sub>3</sub>: C 67.9; H 9.5).

The mother liquor from which the high-melting acid had crystallised was rapidly evaporated to about one third of its original volume and then diluted with five volumes of light petroleum. This treatment precipitated the low-melting *a,a'*-dimethyl-*a,a'*-diisopropylsuccinic acid, m.p. 131–2° (s.c.), unchanged after a further recrystallisation from ethyl acetate-light petroleum (1:5). (Found: C 62.4; H 9.5; equiv. wt 229. Calc. for C<sub>13</sub>H<sub>22</sub>O<sub>4</sub>: C 62.6; H 9.6; equiv. wt 230). The anhydride melted at 78–79° after recrystallisation from light petroleum. (Found: C 67.9; H 9.5. Calc. for C<sub>13</sub>H<sub>20</sub>O<sub>3</sub>: C 67.9; H 9.5). The amounts of pure acids obtained were 1.0 g and 0.7 g, respectively, but the material could be recovered as anhydride from the mother liquor for use in subsequent preparations.

The high-melting *a,a'*-dimethyl-*a,a'*-diisopropylsuccinonitrile was found to correspond to the high-melting acid.

**B. Kolbe method.** The preparation and electrolysis of monoethyl methylisopropylsuccinate was carried out as described previously<sup>2</sup>. The product was obtained in 24 % yield, b.p. 125–130°/4 mm,  $n_D^{20}$  1.4558;  $d_4^{20}$  1.0035. According to analyses it was the dimethyl ester. (Found: C 65.7; H 10.3;  $r_D$  0.2708. Calc. for C<sub>14</sub>H<sub>24</sub>O<sub>4</sub>: C 65.1; H 10.1;  $r_D$  0.2722). The two acids were prepared from this ester in the usual way, m.p. 170–172° (s.c.) and 130–131° (s.c.).

**Attempts to prepare *a,a'*-dimethyl-*a,a'*-di-(*tert.*-butyl)-succinic acid.** The bisazonitrile from pinacolone was prepared according to Overberger *et al.*<sup>11</sup> Decomposition in carbon tetrachloride yielded a dark-brown liquid, which could not be distilled owing to the very vigorous foaming. It was therefore hydrolysed directly with sulphuric acid-water-acetic acid (4:1:3). The product was isolated by ether extraction and distilled, 90–93°/6 mm. The distillate soon solidified and was recrystallised from light petroleum, m.p. 53–57°. According to analyses it was methyl-(*tert.*-butyl)-acetic acid. (Found: C 64.5; H 10.8; equiv. wt 130.6. Calc. for C<sub>7</sub>H<sub>14</sub>O<sub>2</sub>: C 64.5; H 10.9; equiv. wt 130.2). Newman *et al.*<sup>12</sup> reported m.p. 51–52°.

**p*K*-measurements.** The p*K* values for these acids were determined as described in paper III of this series<sup>8</sup>.

The author wishes to express his sincere gratitude to Professor Erik Larsson for his kind interest in this work. A grant from *Matematisk-naturvetenskapliga Fakulteten* is gratefully acknowledged.



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Received November 28, 1959.