

Studies on the Kolbe Electrolytic Synthesis

VII. Electrolysis of Some *t*-Alkylmalonic Half Esters

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In order to demonstrate the competition between radical and carbonium ion processes in the Kolbe electrolysis of α -alkoxycarbonyl acids, *t*-alkylmalonic half esters of the type



have been electrolyzed in methanolic solution. The *t*-alkylalkoxycarbonylmethyl radicals formed from this system dimerize to give a good yield of a mixture of diastereoisomeric 2,3-di-(*t*-alkyl)-succinates. A small amount of a complex mixture of low-boiling non-coupled products is also formed, presumably *via* a carbonium ion mechanism.

An analysis of the NMR-spectra of the 2,3-di-(*t*-alkyl)-succinates demonstrated an interesting case of magnetic non-equivalence between protons in compounds containing asymmetric carbon atoms.

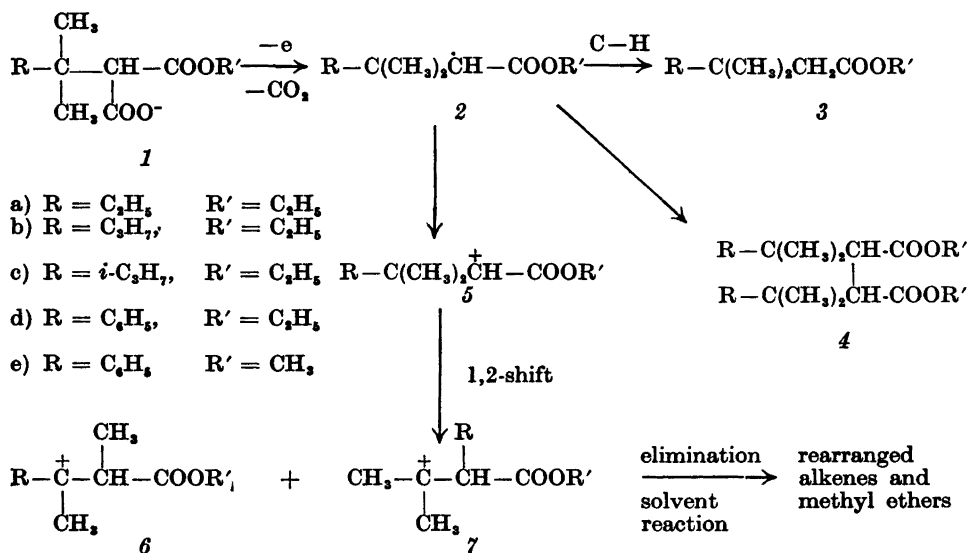
The oxidation of carboxylic acid salts¹ at a platinum anode normally produces a mixture of products formed *via* a radical path (mainly dimer and disproportionation products) and a carbonium ion path (elimination and substitution products). The Kolbe electrosynthesis has traditionally been defined as the preparation of the dimeric product ($RCOO^- \rightarrow R-R + CO_2$) but it has recently been shown that also the carbonium ion process may be utilized for specific synthetic purposes in certain systems.²⁻⁷

Qualitative reasoning based on calculated standard potentials for the possible electrode processes⁸ involved suggests that the dominant factor in determining the ease of oxidation of an anodically generated radical is its ionization potential. A high ionization potential implies a high resistance towards further oxidation at the anode, whereas for radicals with a low ionization potential in many cases only products derived from carbonium ions are observed. It can be estimated empirically that radicals with ionization potentials around 8 eV are borderline cases between these two extremes.

We have previously studied the electrolysis of some acids where the corresponding radicals have or can be assumed to have high ionization potentials

due to stabilization by delocalization of the unpaired electron over an adjacent unsaturated group (COOEt,^{9,10} CN,¹¹ CONH₂¹²) and found that at least fair yields of dimers are obtained in these cases. Very good yields of dimers were obtained from acids where the carbon atom β to the carboxyl group carried no hydrogen atom, *e.g.* monoethyl *t*-butylmalonate,⁹ indicating that besides carbonium ion formation, disproportionation is seriously competing with dimerization of the radicals in cases where this requirement is not fulfilled. The third competing radical reaction would be the attack by the radical on a C—H bond of the solvent or solute molecule but this reaction has been shown to occur only to a minor extent.¹³

This paper is a report on the electrolysis of *t*-alkylmalonic half esters *1*, R = alkyl or phenyl, which, having no hydrogens on the carbon atom β to the carboxyl group, are almost ideal for studying the distribution between radical and carbonium ion products. Apart from the products resulting from radical attack on C—H bonds, the only products formed *via* radicals should be a mixture of meso and racemic dimers. Products originating from the carbonium ion process should be easily recognizable since rearrangement of the intermediate cation should precede product formation (concerning the possibility of radical rearrangements, *cf.* the discussion below). The reaction scheme is outlined below.



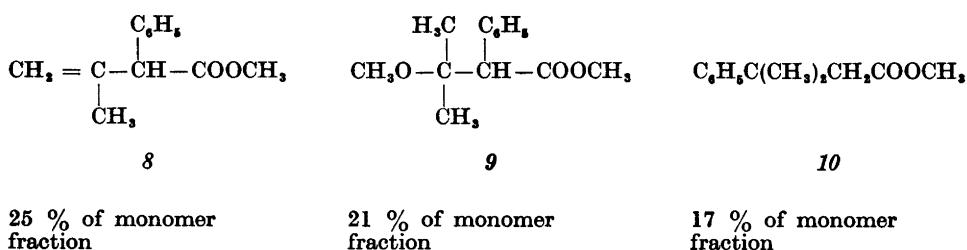
The results have been summarized in Table 1. *t*-Alkylmalonic half esters of type *1* were electrolyzed in methanol under conditions described elsewhere⁹ and the products were crudely separated by distillation into a "monomer" fraction and a fraction of dimeric products. Unfortunately, the monomer fractions in case of R = ethyl, propyl, and isopropyl were too complex (7–10 components with largely overlapping peaks in analytical gas chromatograms) to be separated into components by preparative gas chromatography. Accord-

Table I. Products from the electrolysis of $R(\text{CH}_2)_n\text{C}-\text{CH}-\text{COOEt}$.
 COO^-

R	Yield of monomer fraction % ^a	Total yield of dimeric products (%) ^d	Retention time of dimer min	M.p. of dimer °C	Configuration assignment	Ratio meso/racemic ^b	Calc. C	Calc. H	Analyses Found C	Analyses Found H
C_2H_5	7	74	38.5 ^c	liquid	meso	1.1	68.7	10.9	68.7	10.9
			34 ^c	liquid	racemic		68.7	10.9	69.0	11.0
C_3H_7	16	61	37 ^d	60–62	meso	1.7	70.1	11.2	70.1	11.3
			34 ^d	liquid	racemic		70.1	11.2	69.8	11.2
<i>i</i> - C_3H_7	3	76	215 ^e	63.5–64	meso	0.82	70.1	11.2	70.3	11.3
			160 ^e	liquid	racemic		70.1	11.2	70.0	11.1
C_4H_9	13	48	71/ ^f	153–155	meso	1.9	76.1	8.4	75.8	8.3
			65/ ^f	liquid	racemic					
C_6H_{13} ^g	16 ⁱ	21	31 ^g	165–167	meso	2.0	75.3	7.9	75.4	8.1
			26.5 ^g	108–110	racemic		75.3	7.9	75.1	7.9
CH_3 ^h		85	17.5 ^j	85–87	meso					
			14 ^j	36–40	racemic ^l					

^a Calculated as the alkene, which gives a maximum figure. ^b Determined by gas chromatography on the crude electrolysis mixture. ^c 2 m 20 % UCON-Oil-LB-550-X on Chromosorb P column at 205°. ^d 1 m 20 % apiezon "L" grease on GC-22 column at 180°. ^e Same column as c but at 190°. ^f 2 m 20 % silicon oil DC-200 on Chromosorb P column at 220°. ^g Same column as d but at 240°. ^h Methyl ester. ⁱ From this fraction¹ was isolated δ (25 %), 9 (21 %), and 10 (17 %) by preparative gas chromatography on a 6 m 30 % silicon gum rubber SE-30 on Chromosorb P column at 185°. ^j Same column as c but at 220°. ^k Data partly taken from Ref. 9. ^l Known from resolution experiments on the corresponding diacid.⁹

ingly, only an approximate yield of total monomer is reported in these cases. Nevertheless, it can be concluded that the majority of the components must have formed *via* cationic intermediates, since otherwise the monomer fraction would contain only one product, namely 3. The complexity of the product probably arises from the possibility that either R or methyl may migrate in the Wagner-Meerwein rearrangement, giving rise to cations 6 and 7. For R = phenyl, the situation should be less complex, since phenyl is a much better migrating group than methyl, and accordingly, the monomer fraction should contain fewer components than in the cases of R = alkyl. Indeed this was the case, and it was possible to isolate three out of four compounds from this monomer fraction, one unrearranged and two rearranged products (the methyl ester 1e was electrolyzed in this case in order to simplify the separation and identification):



Compounds 8 and 9 were probably formed from 7 by elimination or reaction with methanol, respectively, whereas 10 was probably formed by attack of the radical 2 on a solvent or solute molecule. The fourth compound was isolated in insufficient amounts to allow identification.

However, it is apparent from Table 1 that the monomer fractions are formed only in small amounts and that the yield of dimers are very good at least when judged by the standards of the Kolbe synthesis. In all cases two diastereoisomers were formed and separated from each other by preparative gas chromatography or adsorption chromatography on alumina. The proportions between the diastereoisomers were determined by analytical gas chromatography under conditions given in Table 1: invariably the high-melting isomer has the longest retention time in the cases where both are solid or one solid and one liquid. For 4, R = ethyl, R' = ethyl, both diastereoisomers are liquid and here the isomer with the longest retention time was classified as the "high-melting" one.

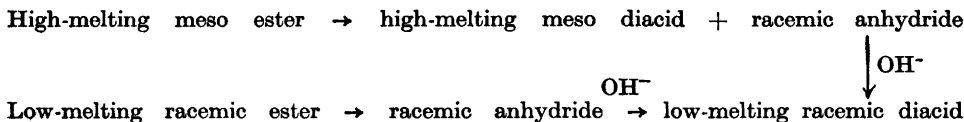
Assignments of relative configuration are based on a comparison of physical properties of 4 and its hydrolysis products with the corresponding properties of meso and racemic diethyl 2,3-di-(*t*-butyl)-succinate and its hydrolysis products.⁹ Here the relative configurations are known from resolution experiments, so that the very characteristic differences between the two diastereoisomers can be used for assignment of configuration in the unknown cases. Meso and racemic diethyl 2,3-di-(*t*-butyl)-succinate is easily hydrolysed by treatment with concentrated sulphuric acid at slightly elevated tempera-

Table 2. NMR-data for dimers (4) obtained by the electrolysis of 1.^{a,b}

R	Configu- ration	Arom. H	Ester CH ₂	Ester CH ₃	-CH- 	(CH ₃)A	(CH ₃)B	$\Delta\delta$	Solvent
C ₂ H ₅ C ₃ H ₇	meso racemic		4.05q 4.05(2q)	1.28t 1.24t	2.77s 2.48s	0.93s 0.98s	0.90s 0.93s	0.03 0.05	CCl ₄ CCl ₄
C ₃ H ₇ C ₃ H ₇	meso racemic		4.06q 4.05(2q)	1.30t 1.24t	2.77s 2.47s	0.95s 0.98s	0.92s 0.93s	0.03 0.05	CCl ₄
<i>i</i> -C ₃ H ₇ <i>i</i> -C ₃ H ₇	meso racemic		4.05q 4.05(2q)	1.30t 1.24t	2.08s 2.72s	1.01s 0.87s	0.81s	0.20 0.87d ^c	CCl ₄ CCl ₄
C ₂ H ₅ C ₆ H ₅	meso racemic	7.25s 7.17s	3.38q 3.37(2q)	0.92t 1.03t	3.28s 2.78s	1.43s 1.38s	1.25s 1.03s	0.18 0.35	CCl ₄ CCl ₄
C ₂ H ₅ ^d C ₃ H ₇ ^d	meso racemic	7.57s 7.22s		2.97s 3.46s	3.35s 2.88s	1.48s 1.38s	1.22s 1.12s	0.26 0.26	CDCl ₃ CDCl ₃
CH ₃ ^d CH ₃ ^d	meso racemic			3.60s 3.59s	2.64s 2.40s				CCl ₄ CCl ₄
CH ₃ CH ₃	meso racemic		4.06q 4.22(2q)	1.30t 1.24t	2.61s 2.38s				CCl ₄ CCl ₄

^a For R = C₂H₅ and C₃H₇, the part of the spectrum originating from R was too complex to be analyzed. ^b s = singlet, d = doublet, t = triplet, q = quadruplet. ^c Signal from methyl in the *i*-C₃H₇ group. ^d Methyl ester.

tures followed by drowning the solution in water according to the following scheme:



The three sets of diastereoisomeric esters 4, R = alkyl, were found to conform to this scheme (see Table 3), although the tendency for the high-melting form to isomerize to give anhydride at the expense of the high-melting diacid is somewhat more pronounced than in the *t*-butyl case.

All of the low-melting diacids, R = alkyl, exhibited very high ratios between K_1 and K_2 in 50 % ethanol (wt/wt), a property which is characteristic for racemic 2,3-dialkylsuccinic acids with bulky alkyl groups.¹⁴ Due to their low solubility, the K_1/K_2 of the high-melting acids could not be determined in this solvent. The analogy in solubility, melting point, anhydri- zation ability and ΔpK values with the *t*-butyl case leaves little doubt that the high-melting acid is the meso form and the low-melting one the racemic one. Accordingly, we assign the high-melting esters (or, for R = ethyl, the isomer with longest retention time in the gas chromatograms) the meso configuration on the basis of the evidence obtained from the hydrolysis products.

For 4, R = phenyl, R' = CH₃ or C₂H₅, the sulphuric acid method failed due to almost complete destruction of the organic material even on careful work. Therefore a new method for hydrolysis of sterically hindered esters, treatment with excess of potassium *t*-butoxide in DMSO¹⁵, was employed. This method worked well but introduced another complication, namely that both forms on hydrolysis gave the same high-melting acid. A check on the two forms of 4, R = *n*-C₃H₇, showed that the same phenomenon occurred again. Apparently one of the diastereoisomeric diacids is markedly more stable in this strongly basic medium. Simple arguments from conformational analytical theory would predict that the stable form would be the meso acid, since only it can have both the bulky alkyl groups and the negatively charged carboxylate groups in a *trans* staggered position. This is in line with the configuration assignments made above. Also, these assignments arrange the diastereoisomers into two sets with characteristically differing features in the NMR-spectrum, which are also observed in the spectra of meso and racemic diethyl 2,3-di-*(t*-butyl)-succinate (see Table 2 and discussion below).

The lower yields of dimer in case of R = C₆H₅, R' = CH₃ or C₂H₅ is probably due to anodic substitution of the phenyl ring. It has previously been shown that aromatic systems are oxidized at the anode¹⁶⁻¹⁸ and in the presence of sodium acetate in acetic acid this leads to acetoxy compounds.^{16,19} In the present case this reaction would lead to the introduction of a methoxyl group in the aromatic ring, which in turn would lower the oxidation potential appreciably and thus facilitate the introduction of a second methoxyl group, *etc.* We also did observe that very high-boiling products remained in appreciable quantities after distilling off the dimer fraction.

Table 3. Properties and analyses of diacids and anhydrides, obtained by hydrolysis of diesters 4, R = alkyl or phenyl.

R	Hydrolysis method ^a	M.p., °C ^b	Configuration assignment	$\Delta pK'$ in 50 % wt/wt ethanol	Analyses			Remark	
					Calc.	Found			
					C	H	C	H	
C ₂ H ₅	A,B	283-284	meso		65.1	10.1	64.9	10.0	diacid
C ₂ H ₅	A	127-128	racemic	7.7	65.1	10.1	64.7	10.1	diacid
C ₂ H ₅ ^d	A	47-48	racemic		70.2	10.0	69.9	10.0	anhydride
C ₃ H ₇	A,B	251-253	meso ^e	7.6	67.1	10.6	66.3	10.5	diacid
C ₃ H ₇	A	156-157	racemic		67.1	10.6	67.4	10.4	diacid
C ₃ H ₇ ^d	A	27	racemic		71.6	10.5	71.4	10.3	anhydride
<i>i</i> -C ₄ H ₉	A,B	290-292	meso	7.4	67.1	10.6	66.8	10.5	diacid
<i>i</i> -C ₄ H ₉	A	160-161	racemic		67.1	10.6	66.7	10.5	diacid
<i>i</i> -C ₄ H ₉ ^d	A	87-88	racemic		71.6	10.5	71.6	10.4	anhydride
C ₆ H ₅	B	309-310	meso ^e		74.5	7.4	74.1	7.6	diacid
CH ₃ / CH ₃	A	295-298	meso	1.86 ^g					diacid
	A	145-147	racemic ^h	9.5 ^g					diacid

^a A = treatment with conc. sulphuric acid, B = treatment with *t*-BuOK in DMSO. ^b Melting points were determined in a sealed capillary according to the directions given in Ref. 9. ^c pK_1 and pK_2 simply taken as the pH values at 1/4 and 3/4 neutralization. ^d Obtained from either high- or low-melting ester by sulphuric acid treatment. ^e Obtained from either high- or low-melting diester by *t*-BuOK-DMSO treatment. ^f See Refs. 9 and 14. ^g Thermodynamic value. ^h Shown by resolution experiments.

No rearrangement had occurred in the dimeric products as judged by NMR-data (see below) and properties of hydrolysis products. 1,2-Phenyl shifts are well documented in the chemistry of free radicals, but 1,2-alkyl shifts do not seem to occur to a detectable extent during the life-time of radicals in liquid phase systems at ordinary temperatures.²⁰ By analogy with the behavior of radicals in homogeneous solution it can be safely concluded that the monomer fractions from the electrolysis of 1, R = alkyl, have been formed almost exclusively *via* the path unrearranged radical (2) → unrearranged carbonium ion (5) → rearranged carbonium ion (6 or 7) → products, whereas the case of R = phenyl is somewhat ambiguous. The rearranged products 8 and 9 might have been formed *via* a rearrangement of the radical followed by anodic oxidation to the carbonium ion. On the other hand, no rearranged dimers could be detected, although radicals of very similar structure are known to give the Kolbe dimers in low yields.²¹ (In principle two diastereoisomers of a singly rearranged dimer and two of a doubly rearranged dimer are possible; these should be easily distinguished by NMR-spectroscopy and/or analysis of hydrolysis products).

Breederveld and Kooyman²² have made a careful investigation of the possibility of a radical rearrangement in the electrolysis of 3-phenylisovaleric acid. This system produces the neophyl radical, which is known to give rearrangement products when generated in homogeneous solution. Breederveld and Kooyman carried out a mixed electrolysis with acetic acid in order to simplify the analysis of products and obtained *t*-amylbenzene as the sole product from the mixed coupling process. Neopentylbenzene, the possible product from a coupling between a rearranged neophyl radical and a methyl radical, was not detected within the limits of IR- and UV-spectroscopy, in this case less than 2 %. The symmetric Kolbe product consisted of at least 90 % bineophyl. The conclusion was that no detectable radical rearrangement took place in this system.

Therefore, we favor a carbonium ion rearrangement in the phenyl case also, although there are no good experimental tests for deciding rigorously between the two possibilities.

The structural analysis of the diesters 4 is based partly on their NMR-spectra. Integrations, chemical shifts and coupling constants compatible with the assigned structures, but not with the possible rearranged ones, were found for the different groups of protons in all cases. The configurational assignments made on the basis of the chemical behavior of the diesters result in an arrangement of the compounds in sets of meso and racemic forms, and it is easily seen from Table 2 that the NMR-spectra also show characteristic differences in the two cases.

First of all, the resonance of the methine proton occurs at lower fields in the meso compounds than in the racemic ones. There is considerable evidence that compounds of this type exist exclusively in a conformation with *trans* *t*-alkyl groups,¹⁴ which would bring the methine hydrogen *gauche* to a carbethoxy in the meso form and *trans* to it in the racemic form. Thus, the methine proton of a meso form would be predicted to give a signal at lower field than that of the racemic form.

Since these molecules contain asymmetric centers, the methyl groups of the *t*-alkyl group and the ester methylene protons have the possibility of being magnetically non-equivalent.^{23,24} As is seen from Table 2, this is the case for the ester methylene protons in the series of racemic compounds but *not in the meso series*. The methyls of the *t*-alkyl group are magnetically non-equivalent in all compounds in the racemic series. The difference between the chemical shifts of the methyls is lower for the meso compounds than for the racemic. Finally, it can be noted that the phenyl group has a much larger influence than alkyl groups on the chemical shift difference, as has been found in other systems.²³

EXPERIMENTAL

Preparation of starting materials. The *t*-butylmalonic diesters were prepared from isopropylidene malonic ester and the appropriate Grignard reagent according to the method given by Golmov and Malevannya²⁵ and Prout *et al.*²⁶ They were first crudely distilled and then redistilled through a helix-packed column of 8 theoretical plates. The purity was checked by gas chromatography and in all cases was better than 99 %.

Since some of our physical data on these compounds do not agree very well with those published earlier,^{25,26} both are given here: Diethyl (2-methyl-2-butyl)-malonate, b.p. 66–71°/0.15 mm, n_D^{20} 1.4319, d_4^{20} 0.9810, reported²⁵ 92°/3 mm, n_D^{20} 1.4320, d_4^{20} 0.9831; Diethyl (2-methyl-2-pentyl)-malonate, b.p. 120–123°/10 mm, n_D^{20} 1.4341, d_4^{20} 0.9703, reported²⁵ 88–89°/1.5 mm, n_D^{20} 1.4352, d_4^{20} 0.9733; Diethyl (2,3-dimethyl-2-butyl)-malonate, b.p. 123–125°/10 mm, n_D^{20} 1.4388, d_4^{20} 0.9836, reported²⁵ b.p. 84°/1.5 mm, n_D^{20} 1.4399, d_4^{20} 0.9913; Diethyl (2-phenyl-2-propyl)-malonate, b.p. 111–113°/0.1 mm, n_D^{20} 1.4931, d_4^{20} 1.064, reported²⁶ b.p. 177–178°/18 mm, n_D^{25} 1.4939, d_4^{25} 1.062; Dimethyl (2-phenyl-2-propyl)-malonate, b.p. 109–114°/0.1 mm, n_D^{20} 1.5056, d_4^{20} 1.107. (Found: C 67.2; H 7.20. Calc. for $C_{14}H_{18}O_4$: C 67.1; H 7.24).

The half esters were prepared by dissolving 0.5 mole of the diester in 200 ml of ethanol, followed by addition of 0.5 mole of potassium hydroxide in 300 ml of ethanol. The solution was boiled under reflux for 4 h after which time it reacted neutrally. The ethanol was distilled off with successive replacement by water. After cooling, the aqueous solution was extracted with ether to remove any unreacted diester, and then acidification with hydrochloric acid liberated the half ester. The ester was taken up in ether and the ether solution was washed with several portions of water. After drying with sodium sulphate the ether was removed in a rotating-film evaporator. The crude half ester was used directly in the electrolysis experiments.

Electrolyses. The electrolyses were carried out as described previously.⁹ The temperature was kept below 30° and the reaction was stopped when the electrolyte had become slightly alkaline.

The reaction mixtures were worked up according to the following procedure: The methanol was partly distilled off and the residual solution cooled, whereby in most cases the high-melting 2,3-di-(*t*-alkyl)-succinate precipitated and could be filtered off. The methanol was then distilled off from the mother liquor and the residue treated with water. The organic material was taken up in ether, the ether solution was washed twice with water and then dried with anhydrous magnesium sulphate. After removing the ether the residue was distilled *in vacuo* through a helix-packed column of 8 theoretical plates. A low-boiling fraction, b.p. lower than 100°/1 mm, was collected (this is the "monomer" fraction referred to above) and then a mixture containing some high- and mostly low-melting diester was collected. This mixture was separated by preparative gas chromatography (for 4, R = Et) or by chromatography on alumina (4, R = C_2H_5 , *i*- C_3H_7 , C_4H_9). The gas chromatographic separation was made on an Autoprep using a 6 m silicon gum rubber S-E30 on Chromosorb P column at 230°. Adsorption chromatography was made on 75 × 2.5 cm alumina columns using carbon tetrachloride and/or benzene as eluents, the high-melting diastereoisomer being eluted first in all cases.

Hydrolysis procedures. A. With concentrated sulphuric acid. High-melting diester, 0.02 mole, was dissolved in concentrated sulphuric acid, 0.2 mole, at room temperature and the solution allowed to stand for 5 min. Then water (a total of 50 ml) was added dropwise. The precipitate was filtered off, washed with water and air-dried. It was boiled with ethyl acetate which left the high-melting diacid undissolved. The high-melting diacid was filtered off and could be recrystallized from acetone or glacial acetic acid.

The mother liquor from the ethyl acetate treatment was evaporated to dryness and the anhydride either isolated or directly hydrolyzed to the low-melting diacid by boiling it with 20 % aqueous potassium hydroxide. The low-melting diacids were recrystallized from benzene, during which it was essential to avoid prolonged heating as anhydridization occurred readily under these conditions.

The low-melting diester was treated in the same way as described above. Ethyl acetate treatment left no high-melting diacid behind, so the anhydride could be worked up directly.

B. With potassium t-butoxide in DMSO. High- or low-melting diester was dissolved in a 1 M solution of potassium t-butoxide (mole ratio ester/base = 1/6) in DMSO and the solution was heated at 100° for 5 h. It was then poured into cold water and the diacid liberated by acidification. This procedure always produced the high-melting diacid, which was proved to be identical with that obtained from hydrolysis procedure A by comparison on infra-red spectra of the samples. Properties and analyses of diacids and anhydrides are given in Table 3.

Separation of products from the monomer fraction after electrolysis of methyl (2-phenyl-2-propyl)-malonate. This fraction was subjected to a preparative gas chromatographic separation on a 6 m 30 % silicon gum rubber SE-30 on Chromosorb P column at 185°. There were four components with retention times 9.2, 9.9, 12.9, and 13.9 min, respectively, from which the first, second, and fourth could be obtained in sufficiently pure state to allow identification. The first component had a medium band at 900 cm^{-1} and a weak one at 1635 cm^{-1} in its IR-spectrum, showing the presence of a =CH₂ group. The NMR-spectrum was compatible with that of methyl 3-methyl-2-phenyl-3-butenate (8), having a singlet of aromatic hydrogens at 7.20, a broad vinyl signal at 4.87, a methine proton singlet at 4.23, a methoxyl group singlet at 3.58, and a somewhat broadened methyl group singlet at 1.70 p.p.m. downfields from TMS in the proportions 5:2:1:3:3.

The second component had an NMR-spectrum in agreement with that expected for methyl 3-methyl-3-phenylbutyrate (10), having a broad singlet of aromatic hydrogens at 7.22, a methoxyl group singlet at 3.47, a methylene group singlet at 2.53 and a methyl group singlet at 1.43 p.p.m. downfields from TMS in the proportions 5:3:2:3. The compound had the same v.p.c. characteristics as an authentic specimen.

The third component could not be isolated in sufficient amount or purity to permit identification.

The fourth component had an NMR-spectrum compatible with that expected for methyl 3-methoxy-3-methyl-2-phenylbutyrate (9), having a multiplet of aromatic hydrogens centered at 7.27, a methine proton signal at 3.71, two methoxyl group singlets at 3.63 and 3.18, and two methyl group signals at 1.27 and 1.09 p.p.m. downfields from TMS (these methyl group hydrogens are magnetically non-equivalent due to the presence of an asymmetric carbon atom) in the proportions 5:1:3:3:3:3.

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