

Incidentally, the ethyl ethylphenylmalonate used in this preparation was obtained from a commercial source and contained some ethyl ethylphenylacetate. This accounts for a by-product obtained in the hydrazine condensation and readily separated by its insolubility in alkali. It melted at 218–219°.

*Anal.* Calcd. for  $C_{20}H_{24}O_2N_2$ : C, 74.07; H, 7.41; N, 8.64. Found [di-(ethylphenylacetyl) hydrazine]: C, 74.24; H, 7.36; N, 8.97.

### Summary

A series of 4,4-dialkyl-3,5-diketopyrazolidines and of 2,6-dialkyl-1,3,5-7-tetraketopyrazo-[1,2- $\alpha$ ]-pyrazoles has been prepared by condensing esters of alkylmalonic acids with hydrazine in the presence of sodium ethoxide.

The esters of dialkylmalonic acids yield the monocyclic pyrazolones, whereas those of monoalkylmalonic acids yield the dicyclic pyrazo-[1,2- $\alpha$ ]-pyrazole derivatives.

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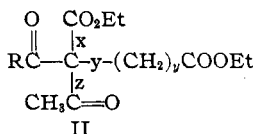
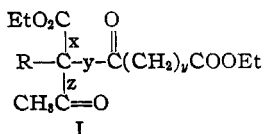
## THE CLEAVAGE OF ALPHA-DIACYL AND OF ALPHA-MONOACYL BETA-KETO DERIVATIVES OF DIETHYL SUCCINATE, GLUTARATE AND ADIPATE

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It has been noted<sup>1</sup> in the hydrolysis of 1,3-diketones and  $\beta$ -keto esters of the types shown in formulas I and II, that cleavage and decarboxylation occurred in such a way as to produce more of the ketone  $RCH_2COCH_3$  than of the keto acid  $RCH_2CO(CH_2)_yCOOH$ , from compounds of type I, and more of the keto acid  $CH_3COCH_2(CH_2)_yCOOH$  than of  $RCOCH_2(CH_2)_yCOOH$  from compounds of type II. That is to say, the removal of the acetyl group occurred to a less extent from compounds of type I, and to a greater extent from compounds of type II, than is desirable from the standpoint of the synthesis from acetoacetic ester of high molecular weight keto acids.



It may clarify the ensuing discussion if it is pointed out that compounds of these two types may upon hydrolysis cleave at three points

<sup>1</sup> G. M. Robinson and R. Robinson, *J. Chem. Soc.*, 175 (1925); G. M. Robinson, *ibid.*, 745 (1930).

in the molecule as indicated by "x," "y" and "z." The "x" linkages are stable toward ethanol so that alcoholysis occurs at only "y" or "z." The "x" linkage is labile toward hydrolysis and is cleaved along with either "y" or "z." Thus there may be produced either by alcoholysis or hydrolysis two sets of products depending upon whether "y" or "z" is the more reactive linkage.

It has been observed in this Laboratory<sup>2</sup> that the ratio of the two possible sets of products obtained in the cleavage of unsymmetrical 1,3-diketones is dependent upon the environment during cleavage as well as upon the structure of the diketones. It therefore seemed desirable to apply to the compounds of types I and II the following methods of cleavage: (1) alcoholysis at 60° and under one atmosphere pressure using hydrogen chloride as a catalyst; (2) alcoholysis at 150–250°, under 100 atmospheres, using traces of water or aluminum ethoxide as catalysts; (3) hydrolysis at 150–250° under 100 atmospheres.

For this purpose two compounds of type I, *i. e.*, diethyl  $\alpha$ -*n*-butyl- $\alpha$ -acetyl- $\beta$ -keto-adipate ( $R=C_4H_9$ ,  $y=2$ ) and diethyl  $\alpha$ -*n*-lauryl- $\alpha$ -acetyl- $\beta$ -keto-adipate ( $R=C_{12}H_{25}$ ,  $y=2$ ) and five compounds of type II, *i. e.*, diethyl  $\alpha$ -benzoyl- $\alpha$ -acetyl-succinate ( $R=C_6H_5$ ,  $y=1$ ), diethyl  $\alpha$ -benzoyl- $\alpha$ -acetylglutarate ( $R=C_6H_5$ ,  $y=2$ ), diethyl  $\alpha$ -*n*-butyryl- $\alpha$ -acetylsuccinate ( $R=C_3H_7$ ,  $y=1$ ), diethyl  $\alpha$ -*n*-butyryl- $\alpha$ -acetylglutarate ( $R=C_3H_7$ ,  $y=2$ ) and diethyl  $\alpha$ -trimethylacetyl- $\alpha$ -acetylglutarate ( $R=tert.-C_4H_7$ ,  $y=2$ ) have been subjected to various conditions inducing cleavage. In addition the alcoholysis of diethyl  $\alpha$ -acetylsuccinate and glutarate was studied in order to ascertain the behavior on cleavage of these monoacyl esters which might be intermediate products of the diacylsuccinic and glutaric esters of type II.

**Alcoholysis of Keto Esters in Presence of Hydrogen Chloride.**—There are recorded in Table I representative data obtained in subjecting  $\alpha$ -acetylsuccinic and glutaric,  $\alpha$ -acetyl- $\alpha$ -butyrylsuccinic and glutaric and  $\alpha$ -acetyltrimethylacetylglutaric esters to alcoholysis at 60° in the presence of hydrogen chloride. The procedures were essentially the same as those previously described.<sup>3</sup> In brief the data show that the acetylglutaric and especially the succinic esters are rather inactive toward ethanol at 60° even in the presence of a high concentration of hydrogen chloride. (It may be recalled that acetoacetic ester itself is not cleaved at all under these conditions.) The diacylsuccinic and glutaric esters undergo more than 80% alcoholysis under these same conditions, the ratio of cleavage being such that in the case of the succinate the ratio of acetyl to butyryl cleavage is approximately 1 to 2 while with the glutarate it is about 1 to 4. The acetyltrimethylacetylglutaric ester is much more resistant to alcoholysis

<sup>2</sup> Connor and Adkins, *THIS JOURNAL*, **54**, 3420 (1932).

<sup>3</sup> Kutz and Adkins, *ibid.*, **52**, 4036 (1930).

TABLE I  
 ALCOHOLYSIS OF KETO ESTERS IN PRESENCE OF HYDROGEN CHLORIDE<sup>a</sup>

Diethyl ester of	Millimoles		Cleavage	
	Ester	HCl	Acetyl	% total
$\alpha$ -Acetylsuccinate	10	25	..	11
$\alpha$ -Acetylsuccinate	10	50	..	9
$\alpha$ -Acetylglutarate	6.5	25	..	19
$\alpha$ -Acetylglutarate	6.5	50	..	20
$\alpha$ -Acetyl- $\alpha$ -butyrylsuccinate	10	12	35	83
$\alpha$ -Acetyl- $\alpha$ -butyrylsuccinate	10	25	35	85
$\alpha$ -Acetyl- $\alpha$ -butyrylglutarate	5	50	16	83
$\alpha$ -Acetyl- $\alpha$ -butyrylglutarate	5	12	21	83
$\alpha$ -Acetyl- $\alpha$ -trimethylacetylglutarate	5	25	31	46

<sup>a</sup> Temperature 60°, time 96–120 hours, 435 millimoles of ethanol. An extensive study had shown that if the ratio of hydrogen chloride to ester was lower than indicated in the table, alcoholysis was slow and incomplete. Higher ratios of catalyst did not facilitate the reaction. If the temperature was as high as 68°, ethyl chloride was formed and no advantages were secured.

than the diacyl ester having only normal chains while the ratio of cleavage products is correspondingly more favorable to acetyl cleavage. That is to say, the amount of acetyl cleavage in a given length of time is approximately the same (14 to 17%) for acetyltrimethylacetylglutaric as it is or acetylbutyrylglutaric ester while the non-acetyl cleavage is much less for the trimethylacetyl (35%) than for the butyryl (66%).

**Alcoholysis at 150–200°.**—There is recorded in Table II a summary of the data obtained in subjecting four acyl substituted succinic and glutaric esters to the action of ethanol at 150–250° under a pressure of approximately 100 atmospheres. The procedure was essentially the same as that described.<sup>2</sup>

The data show that diethyl  $\alpha$ -acetylsuccinic ester is quite stable at 150° in the presence of ethanol dried over aluminum ethoxide, and that it is cleaved to the extent of only 11% with ethanol dried over lime only. Aluminum ethoxide is a catalyst for the alcoholysis of this  $\beta$ -keto ester as has been previously observed for the simple 1,3-diketones. Diethyl  $\alpha$ -acetyl- $\alpha$ -*n*-butyrylglutarate was considerably more resistant to alcoholysis than was the corresponding succinate as shown by the fact that under similar conditions the former was cleaved to the extent of only 11% while the latter showed 56% alcoholysis, the extent of cleavage being measured by the amount of ethyl acetate (determined as acetic acid) produced by alcoholysis.

The diacylsuccinic and glutaric esters, since they are 1,3-diketones as well as  $\beta$ -keto esters, are cleaved more rapidly and at a lower temperature than are the monoacyl esters. This is indicated by the fact that alcohol dried with aluminum ethoxide brought about 91% alcoholysis of acetylbutyrylsuccinic ester within ten hours, while under the same conditions

the monoacetylsuccinic ester was cleaved to the extent of only 4%. The ratio of cleavage of acetyl to butyryl cleavage was approximately 2 to 3. The diacetylsuccinate is more rapidly cleaved than is the glutarate. The proportion of acetyl cleavage for the glutarate is lower, being approximately 1 to 4.

TABLE II  
ALCOHOLYSIS AND HYDROLYSIS OF KETO ESTERS AT 100 ATMOSPHERES PRESSURE

Diethyl ester of	Millimoles		Temp., °C.	Cleavage		
	Ester	Re-agent		Acetyl m.moles	%	Total
$\alpha$ -Acetylsuccinate	40	200 EtOH <sup>a</sup>	200	..	..	56 <sup>d</sup>
$\alpha$ -Acetylsuccinate	40	200 EtOH <sup>a</sup>	150	..	..	11 <sup>d</sup>
$\alpha$ -Acetylsuccinate	40	200 EtOH <sup>b</sup>	150	..	..	74 <sup>d</sup>
$\alpha$ -Acetylsuccinate	40	200 EtOH <sup>c</sup>	150	..	..	4 <sup>d</sup>
$\alpha$ -Acetylglutarate	40	200 EtOH <sup>a</sup>	200	..	..	11 <sup>d</sup>
$\alpha$ -Acetyl- $\alpha$ -butyrylsuccinate	40	200 EtOH <sup>c</sup>	150	..	56	58 <sup>d</sup>
$\alpha$ -Acetyl- $\alpha$ -butyrylsuccinate	100	1400 EtOH <sup>c</sup>	150	..	41	91 <sup>d</sup>
$\alpha$ -Acetyl- $\alpha$ -butyrylsuccinate	100	1000 H <sub>2</sub> O	150	25.0 <sup>f</sup>	..	<sup>e</sup>
$\alpha$ -Acetyl- $\alpha$ -butyrylsuccinate	200	3447 H <sub>2</sub> O	150	50.0 <sup>f</sup>	..	<sup>e</sup>
$\alpha$ -Acetyl- $\alpha$ -butyrylglutarate	100	500 EtOH <sup>a</sup>	150	..	20	41 <sup>d</sup>
$\alpha$ -Acetyl- $\alpha$ -butyrylglutarate	100	1000 H <sub>2</sub> O	200	0	..	<sup>e</sup>
$\alpha$ -Acetyl- $\alpha$ -butyrylglutarate	100	1217 H <sub>2</sub> O	200	1	..	<sup>e</sup>
$\alpha$ -Acetyl- $\alpha$ -trimethylacetylglutarate	94	940 H <sub>2</sub> O	200	1	..	<sup>e</sup>

<sup>a</sup> Ethanol dried over lime. <sup>b</sup> Ethanol contained 4.3 millimoles of Al(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> per 100 millimoles of ethanol. <sup>c</sup> Ethanol dried over aluminum ethoxide. <sup>d</sup> Ten hours. <sup>e</sup> 26 to 39 hours. <sup>f</sup> The ratio of acetyl to butyryl cleavage on the basis of the ratio of acetic to butyric acid obtained indicated that the acetyl cleavage was 39–40% of the total.

**Hydrolysis of Esters at 150–200°.**—There is also recorded in Table II a summary of the data obtained as the result of subjecting  $\alpha$ -acetyl- $\alpha$ -butyrylsuccinic,  $\alpha$ -acetyl- $\alpha$ -butyrylglutaric and  $\alpha$ -acetyl- $\alpha$ -trimethylacetylglutaric esters to hydrolysis at 150–200°. The hydrolysis of diacetylsuccinic and glutaric esters differs in two respects from their alcoholysis. Decarboxylation as well as hydrolysis occurs and there is produced a mixture of four acids and their esters.

Decarboxylation is complete after eight or ten hours and probably within a very much shorter time. This is shown by the fact that at the end of the first period of hydrolysis (eight to ten hours) the pressure was approximately fifteen atmospheres higher than before the hydrolysis, while in subsequent periods there was no such increase in pressure. Furthermore, there is a weight loss observed after the first period of hydrolysis which corresponds to the loss of one molecule of carbon dioxide by one molecule of the diacyl ester. For example, the weight loss in runs which did not involve decarboxylation were of the order of 0.9 g., while the losses in three runs in which decarboxylation did occur were 4.94, 4.69, 5.60, respectively. The difference between the average of these values and the normal weight

loss is close to the weight of carbon dioxide (4.4 g.) which should have been produced.

The greater number and higher boiling points of some of the components of the hydrolysis mixture (as compared with the mixture from alcoholysis) made it impossible to obtain as accurate an evaluation of the ratio of volatile acids produced as has been hitherto possible. It is, of course,

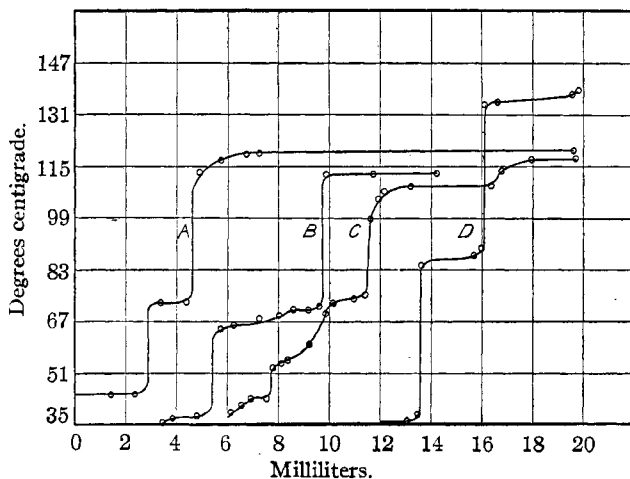


Fig. 1.—Distillation curves of products of hydrolysis (A, B and C at 3–4 mm., D at 14–15 mm.). A. Diethyl  $\alpha$ -acetyl- $\alpha$ -butyrylglutarate: butyric acid, 41°, neut. equiv. 89, calcd. 88; ethyl  $\Delta$ -ketoheptanoate 73°, sapon. equiv. 149, calcd. 158;  $\Delta$ -ketoheptanoic acid, 120°, neut. equiv. 133, calcd. 130. B. Diethyl  $\alpha$ -acetyl- $\alpha$ -trimethylacetylglutarate: trimethylacetic acid, 38°, (solid) neut. equiv. 105, calcd. 102; ethyl  $\Delta$ -ketoheptanoate, 72°, sapon. equiv. 156;  $\Delta$ -ketoheptanoic acid, 113°, neut. equiv. 134. C. Diethyl  $\alpha$ -acetyl- $\alpha$ -butyrylsuccinate: butyric,  $\gamma$ -ketovaleric,  $\gamma$ -ketoheptanoic and the esters of the two latter were present but no clear cut separations were obtained. D. Diethyl  $\alpha$ -acetyl- $\alpha$ -butyrylsuccinate (hydrolysis product saponified and dry acids obtained before fractionation): acetic, 36°, butyric, 87°,  $\gamma$ -ketovaleric, 136°, neut. equiv. 119, calcd. 116;  $\gamma$ -ketoheptanoic 150°, m. p. 43–45° (m. p. 46–47°) Bouveault and Bongert, *Bull. soc. chim.*, [3] 27, 1088 (1902).

feasible to distil out the acetic acid and ethyl acetate produced, but it was not found possible to distil all the butyric acid out of the hydrolysis mixture, after it had been made up to standard volume with ethanol in the standard procedure. However, the analytical results obtained show very clearly the differences in the behavior of the three diacyl esters under consideration.

Diethyl  $\alpha$ -acetyl- $\alpha$ -butyrylsuccinate cleaved so that the amount of

the acetyl cleavage was between 25 and 40% of the total cleavage. The two diacylglutarates gave little, if any, acetyl cleavage and in the case of acetyl-*n*-butyryl ester there was *no trace* of acetic acid formed.

The conclusions based on distillation and partition of the acids are amply supported by the results obtained through the distillation of the residual higher boiling portion of the hydrolysis product. The distillation curves of these products are given in Fig. 1. For example, from acetylbutyrylglutaric ester there were obtained about 3 g. of butyric acid, about 2 g. of  $\Delta$ -keto-hexanoic acid and about 14 g. of its ethyl ester. Similarly the distillation of the hydrolysis product from  $\alpha$ -acetyl- $\alpha$ -trimethylacetylglutaric ester gave a small amount of trimethylacetic acid and the remainder was  $\Delta$ -keto-hexanoic acid and its ethyl ester. (The greater portion of the butyric and trimethylacetic acids had been previously distilled out of the hydrolysis product in subjecting it to the standard procedure for the determination of the amount and ratio of volatile acids.)

The distillation of the higher boiling products from the hydrolysis of acetylbutyrylsuccinic ester did not give as clear cut results as has been noted above for the glutaric esters. This is true because both  $\gamma$ -ketovaleric (levulinic) acid and ester and  $\gamma$ -keto-heptanoic acid and ester were produced. However, the largest fraction was that containing  $\gamma$ -ketovaleric acid and its ester as would be expected upon the basis of the fact that the butyryl predominated over the acetyl cleavage. The relative ratio of these two cleavages is further evidenced by the distillation curve for the acids obtained after saponification of the mixture of esters. There were obtained 3.4 g. of  $\gamma$ -ketovaleric and 2.4 g. of  $\gamma$ -keto-heptanoic. The ratio of acetic and butyric acids obtained is not significant since the loss of the more water-soluble acids is greater.

TABLE III  
HYDROLYSIS OF CERTAIN KETO ESTERS (25 HRS., 100 ATM., AT 200°)

Name of ester	Ester, g.	Water, g.	Yield of products
Diethyl $\alpha$ -acetyl- $\alpha$ -benzoylsuccinate	13	7.3	$\beta$ -Benzoylpropionic acid 69%; acetic acid 64%; benzoic acid 31%
Diethyl $\alpha$ -acetyl- $\alpha$ -benzoylglutarate	16.7	7.2	$\beta$ -Benzoylbutyric acid 79%; acetic acid 80%; benzoic acid 21%
Diethyl $\alpha$ -acetyl- $\alpha$ - <i>n</i> -butyl- $\beta$ -keto- adipate	28.2	18.0	$\gamma$ -Keto-nonanoic acid 18%; acetic acid 45%; heptanone-2 59%
Diethyl $\alpha$ -acetyl- $\alpha$ - <i>n</i> -lauryl- $\beta$ -keto- adipate	10.6	4.6	$\gamma$ -Keto-margaric acid 33%; acetic acid 30%; tridecanone-2 66%

There is given in Table III a summary of the yields of products obtained from the hydrolysis of a diacylsuccinate and glutarate, and from two acyl alkyl keto adipates. These data show that the acetyl cleavage greatly predominated over the benzoyl cleavage for the succinate and the

glutarate. In the case of the substituted adipates the formation of succinic acid predominated over that of acetic acid. For the butyl derivative the cleavage at the "z" linkage of formula 1 was in the ratio of 3 to 4 at the "y" linkage, while for the lauryl derivative the cleavage at "z" was less than 1 as compared to 2 at the "y" linkage. The figures just given for the butyl derivative would lead one to expect somewhat greater yields of the keto nonanoic acid than was obtained. However, the yield of keto-margaric acid was in good agreement with the cleavage of the "y" linkage as measured by the yield of tridecanone-1.

### Experimental Part

The procedure followed in working up the products of the hydrolyses referred to in Table III was as follows. The reaction product from the succinate was refluxed for one hour with 100 ml. of a 1.37 *N* solution of sodium hydroxide. The mixture was cooled and acidified with 92 ml. of a 1.52 *N* sulfuric acid solution. The resulting crystals of benzoic and  $\beta$ -benzoylpropionic acid were filtered off after the mixture had been cooled in an ice-salt mixture. The crystals were washed with ice cold water, and after drying weighed 6.5 g. A titration in alcohol of a sample of this mixture of solid acids gave a value of 160.5 for the average molecular weight. This corresponds to a mixture of 31.3% benzoic and 68.7%  $\beta$ -benzoylpropionic acid. The mixture of acetic and levulinic acids which remained in solution when the solid acids were precipitated was fractionated from a modified Claisen flask until 175 ml. of distillate was obtained. Seventy-five ml. of water was then added to the residue and distilled out. The combined distillates were then made up to 250 ml. and an aliquot titrated. The amount of acetic acid found was 0.026 mole, which corresponds to a yield of 64%.

The hydrolysis product from the glutarate was treated in the same manner as that from the succinate. There was obtained 8.9 g. of solid acids, neutral equivalent 177, which corresponds with 21.4% benzoic acid and 78.6%  $\beta$ -benzoylbutyric acid. The yield of acetic acid (0.04 mole) was 80% of the theoretical amount. The hydrolysis product from diethyl  $\alpha$ -acetyl- $\alpha$ -*n*-butyl- $\beta$ -keto-adipate was saponified as in the case of the succinate and glutarate. The ketone was extracted with ether, the solution dried over sodium sulfate. Fractionation of the material gave 6.4 g. of heptanone-2, b. p. 143–146 (740 mm.). The aqueous solution of the salts of the acids was then concentrated to one-half its volume and acidified, and, after cooling, the 8.2 g. of solid acids was filtered off. The mixture of succinic and  $\gamma$ -keto-nonanoic acids was then shaken in 25 ml. of ether. The succinic acid is insoluble in ether and 5.2 g. was obtained.  $\gamma$ -Ketononanoic acid (2.8 g.), m. p. 69–69.5°, was obtained from the ether solution. The neutral equivalent was found to be 172.5; the calculated is 172.

*Anal.* Calcd. for  $C_9H_{16}O_5$ : C, 62.79; H, 9.30. Found: C, 62.83; H, 9.21.

The amount of acetic acid found by distillation was 44.7% of the theoretical.

The hydrolysis products from diethyl  $\alpha$ -acetyl- $\alpha$ -lauryl- $\beta$ -keto-adipate were worked up in a similar fashion. Tridecanone-2 (3.7 g.), m. p. 39–40°,  $\gamma$ -keto-margaric acid (2.3 g.), m. p. 97–98° and 0.4 g. of acetic acid were obtained. The neutral equivalent of the  $\gamma$ -keto-margaric acid was found to be 288, calcd. 284.

*Anal.* Calcd. for  $C_{17}H_{32}O_5$ : C, 71.83; H, 11.26. Found: C, 72.02; H, 11.18.

Certain data and information in regard to the preparation of the reagents used in the experiments on alcoholysis and hydrolysis are given in Table IV and in the footnotes to Table IV.

TABLE IV  
PREPARATIONS OF REAGENTS

Products and methods	Yield g. %	Reactants		E.	F.	$d_{25}^{25}$	$n_D^{20}$	Boiling range °C. Mm.	Carbon, % Calcd.	Hydrogen, % Found
		E.	F.							
Diethyl $\alpha$ -acetylsuccinate <sup>a</sup>	173	Acetoacetic ester	130	Ethyl chloroacetate <sup>i</sup>	122			121-123	4-5	
Diethyl $\alpha$ -acetylglutarate <sup>a</sup>	120	Acetoacetic ester	130	Ethyl $\beta$ -bromopropionate <sup>j</sup>	181			132-134	3-4	
Ethyl $\alpha$ -benzoyl- $\alpha$ -acetylacetate <sup>b</sup>	118	Acetoacetic ester	100	Benzoyl chloride	109			165-167	10	
Diethyl $\alpha$ -acetyl- $\alpha$ -butyrylsuccinate <sup>c</sup>	30	succinate	43.2	<i>n</i> -Butyryl chloride	21.3	1.0793	1.4460	184-150	4	58.77 58.22 58.07 7.75 7.69 7.70
Diethyl $\alpha$ -acetyl- $\alpha$ -benzoylsuccinate <sup>d</sup>	89	succinate	108	Benzoyl chloride	70	1.145	1.5021	178-182	1	63.73 63.69 63.41 6.27 6.35 6.30
Diethyl $\alpha$ -acetyl- $\alpha$ -benzoylsuccinate <sup>d</sup>	44	benzoylacetate	58	Ethyl chloroacetate	31			180-184	1-2	
Diethyl $\alpha$ -acetyl- $\alpha$ -benzoylglutarate <sup>d</sup>	95	glutarate	115	Benzoyl chloride	70	1.1426	1.4990	184-187	1	64.69 64.75 64.85 6.69 6.73 6.76
Diethyl $\alpha$ -acetyl- $\alpha$ - <i>n</i> -butyrylglutarate <sup>e</sup>	31	glutarate	46	<i>n</i> -Butyryl chloride	22	1.0621	1.4420	156-159	3	59.96 59.76 59.67 8.05 8.11 8.10
Diethyl $\alpha$ -acetyl- $\alpha$ -trimethylacetylsuccinate <sup>e</sup>	20	succinate		Trimethylacetyl chloride		1.0533	1.4478	143-146	4-5	59.96 59.64
Diethyl $\alpha$ -acetyl- $\alpha$ -trimethylacetylglutarate <sup>e</sup>	21	glutarate		Trimethylacetyl chloride		1.0502	1.4506	148-153	4-5	61.11 60.70 60.81 8.34 8.26 8.31
Diethyl $\alpha$ -acetyl- $\alpha$ - <i>n</i> -butylacetylglutarate <sup>e</sup>	68	glutarate	94	$\beta$ -Carbethoxypropionyl chloride <sup>g</sup>	77	1.0639	1.4501	147-150	1	61.14 60.93
Diethyl $\alpha$ -acetyl- $\alpha$ - <i>n</i> -butylacetylglutarate <sup>e</sup>	28	glutarate	46	$\beta$ -Carbethoxypropionyl chloride	20	0.9810	1.4515	234-239	1	67.60 67.83 67.62 9.86 9.88 9.89

<sup>a</sup> Sodium (23 g.) was slowly added to 400 ml. of anhydrous alcohol, contained in a 3-necked, 3-liter flask fitted with a dropping funnel, a reflux condenser and a stirrer. The reaction mixture was heated on a steam-bath to complete the reaction. One hundred and thirty grams of acetoacetic ester was then slowly added followed by 122 g. of ethyl chloroacetate (or the equivalent amount of ethyl  $\beta$ -bromopropionate). The reaction mixture was then refluxed for four hours after the addition of the ester, the mixture cooled, centrifuged, the salt layer washed with alcohol and again centrifuged. The alcohol was removed by fractionation from a modified Claisen flask, and the esters carefully fractionated at 4-5 mm. through a Widmer column having a glass spiral 20 mm. in length.

<sup>b</sup> Claisen's<sup>4</sup> procedure apparently gave a better product than did that of Shirner and Schmidt,<sup>5</sup> when the temperature of the reaction mixture was kept below 10° as recommended by Claisen.

<sup>4</sup> Claisen, *Ann.*, **291**, 67 (1896).

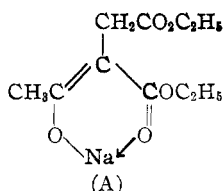
<sup>5</sup> Shirner and Schmidt, *This Journal*, **51**, 3637 (1929).



<sup>c</sup> Sodium (4.6 g.) was powdered under xylene, thoroughly washed with ether, suspended in 240 ml. of ether, and 43.2 g. of ethyl  $\alpha$ -acetylsuccinate (or an equivalent amount of the acylglutarate or alkyl acetoacetic ester) slowly added from a dropping funnel while the reaction mixture refluxed. *n*-Butyryl chloride (21.3 g.) (or an equivalent amount of another acid chloride) was slowly added to the rapidly stirred and gently refluxing mixture. The reaction mixture was then allowed to cool to room temperature and to stand with stirring for ten hours. It was then heated on a steam-bath, stirred and refluxed overnight. The salt was removed by centrifuging, the ether by distillation, and the esters were fractionated through a Widmer column.

<sup>d</sup> This ester was made by essentially the same procedure as has been described in (c) except that the distillation of the product was made at 1 mm. from a Wood's metal bath kept at 205–220°. Bumping was prevented by the use of capillary tubes sealed off at the upper end, since it is very important that no air be allowed to enter the distillation flask.

<sup>e</sup> This ester was prepared by the same procedure as described in (c) and (d) except that it was necessary (due to the insolubility in ether of the sodium derivative) to stir the  $\alpha$ -acylglutarate for ten hours with sodium in order to complete the reaction. The sodium derivative of diethyl  $\alpha$ -acetylsuccinate is soluble in ether while that of the corresponding glutarate is insoluble in ether. This means, according to Sidgwick's views on the sodium derivative of 1,3-diketones, that the sodium derivative of the succinate is in ether, a covalent chelate compound of formula (A), while the glutarate is a simple salt.<sup>6</sup>



formula (A), while the glutarate is a simple salt.<sup>6</sup>

<sup>f</sup> "Organic Syntheses," John Wiley and Sons, New York, 1923, Vol. III, p. 51.

<sup>g</sup> Blaise, *Bull. soc. chim.*, [3] 21, 641 (1899).

<sup>h</sup> "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 36.

<sup>i</sup> Conrad, *Ann.*, 188, 217 (1877), 556 g. of ester was obtained from 600 g. of acid.

### Summary

This study of the ratio of cleavage products in the alcoholysis and hydrolysis of five  $\alpha,\alpha$ -diacylsuccinic and glutaric esters, and of two  $\alpha$ -acetyl- $\alpha$ -alkyl- $\beta$ -keto-adipic esters has brought to light a number of facts with regard to the relative stability and mode of cleavage of these compounds. However, the number of compounds studied is too few to more than indicate the complexity of the factors which determine the ratio of cleavage products. It is clear, however, that the ratio of products from these compounds is not determined by the relative acidity of the acids produced by cleavage. This is shown by the fact that the ratio of acetic to benzoic acid was 2 to 1 for the hydrolysis of acetylbenzoylsuccinic ester and 4 to 1 for the corresponding glutaric ester. Similarly, the ratio of acetic acid to butyric acid was approximately 2 to 5 for acetylbutyrylsuccinic ester while from acetylbutyrylglutaric ester no acetic acid was produced. The effect of the size of the alkyl group is also pronounced as is evidenced by the fact that the acetyl cleavage was only two-thirds as much in  $\alpha$ -lauryl- $\alpha$ -acetyl- $\beta$ -keto-adipic ester as it was in the corresponding

<sup>6</sup> Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1929, p. 145–151; Sidgwick and Brewer, *J. Chem. Soc.*, 127, 2379 (1925).

butyl compound. A number of conclusions previously arrived at with regard to the cleavage of simple 1,3-diketones have been found also to hold for these more complex 1,3-diketones which are also  $\beta$ -keto esters.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

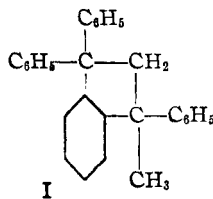
## THE ABSORPTION SPECTRUM OF METHYLDIPHENYL-CHLOROMETHANE PLUS STANNIC CHLORIDE. THE PREPARATION OF 9,10-DIPHENYLPHENANTHRENE FROM TETRAPHENYLETHYLENE DICHLORIDE<sup>1</sup>

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In an earlier communication<sup>2</sup> it was shown that 1,1,3-triphenyl-3-methylhydrindene (I) is obtained in practically quantitative yield by adding anhydrous stannic chloride to a benzene solution of methyldiphenylchloromethane at room temperature. It was also shown that the reaction is a general one and can be used with other alkylarylmethyl halides and that other reagents such as antimony pentachloride, aluminum chloride, etc., can replace the stannic chloride. The reaction mechanism which was suggested postulated the formation of a quinonoid salt as an intermediate step, and in support of this assumption it was noted that the reaction is always accompanied by a transitory color and that the reagents used are those which are known to produce quinoidation of the triarylmethyl halides.



Preliminary absorption spectra measurements in the visible region failed to establish the identity of the intermediate colored compound or compounds since the point of maximum absorption was found to lie beyond the range of the visual apparatus. Spectrographic measurements of the absorption in the ultraviolet region have now been made which confirm the existence of a quinonoid modification of methyldiphenylchloromethane in the reaction mixture.

The quantitative absorption curves for methyldiphenylcarbinol, methyldiphenylchloromethane and asymmetrical diphenylethylene are shown in Fig. 1. (The curve for diphenylethylene was determined inasmuch as this compound is readily formed by loss of hydrogen chloride from methyldiphenylchloromethane.) The curves for the carbinol and the chloride

<sup>1</sup> This paper represents the second part of a dissertation submitted to the Graduate School by Mr. Ryan in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

<sup>2</sup> Schoeffle and Ryan, *THIS JOURNAL*, **52**, 4021 (1930).