

zation had begun in a month and by the end of three months the whole mass was solid. By recrystallization from ether-petroleum ether the melting point was raised from 124–129° to 133–134°. The mixed melting point with an authentic sample of the 134° hydroxy acid XIIb showed no depression and the infrared spectra of the two were identical.

Cyclohexane Carboxylic Acid Anhydride.—Fifteen grams of cyclohexane carboxylic acid (0.117 mole), 30 g. (0.294 mole) of acetic anhydride, and 0.5 ml. of concentrated hydrochloric acid were heated on a steam-bath for six hours. The solution became black. It was fractionally distilled and the portion boiling at 140–146° (5 mm.) was collected. This

was twice more fractionally distilled and the center portion boiling at 142–143° (5 mm.) was collected; $n_{25}^{20}D$ 1.4748.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 71.05; H, 9.14.

This anhydride has been prepared previously by Lumsden¹⁸ from sodium hexahydrobenzoate and hexahydrobenzoyl chloride; b.p. 280–283°, M_{Na}^{15} 1.48189.

(18) J. S. Lumsden, *J. Chem. Soc.*, **87**, 90 (1905).

CAMBRIDGE 38, MASSACHUSETTS

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[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER & GAMBLE CO.]

The Polymorphism of 2-Acetyl-, 2-Butyryl- and 2-Caproyldistearin and -dipalmitin

By F. L. JACKSON, R. L. WILLE AND E. S. LUTTON

A study of polymorphism by thermal and diffraction methods is reported for six symmetrical diacid triglycerides in which the 2-position is occupied by a very short chain. Solid forms observed were as follows: for 2-acetyldistearin and 2-acetyldipalmitin—sub-alpha-1 and beta-3; for 2-butyryldistearin and 2-butyryldipalmitin—sub-alpha-1, alpha-1, superalpha-1, and beta-3; for 2-caproyldistearin and 2-caproyldipalmitin—sub-B-beta-3, sub-A-beta-3 and beta-3 and also sub-alpha-1 for the former glyceride but sub-alpha-3 for the latter. The polymorphism of these compounds thus shows several hitherto unreported features—specifically the sub-alpha-1, alpha-1 and super-alpha-1 forms and the multiplicity of beta-type forms for the caproyl glycerides. Such abnormalities in behavior presumably result from the relatively large role played by the carbonyl portions of the short acyl groups.

In previous communications from this Laboratory, the thermal and X-ray diffraction characteristics of certain mixed saturated diacid triglycerides were discussed.^{1–4} These compounds show considerable uniformity of polymorphic behavior by exhibiting, in most cases, the three forms—alpha, beta prime and beta—each with a characteristic melting point. Outstanding individuality is shown by 2-stearoyldipalmitin² and 1-palmitoyldibehenin⁴ which fail to show a beta form, and by 2-myristoyldistearin which shows four forms (alpha-2, beta prime-2, beta prime-4 and beta-3 forms¹). In addition, the unsymmetrical dibehenyl triglycerides show a new sub-alpha form⁴ which transforms reversibly to alpha.

The shortest chain in glycerides previously prepared in this Laboratory was lauryl,⁵ and Malkin in his extensive studies of mixed glyceride polymorphism did not deal with shorter chains than capryl.^{5,6} In the present paper there are discussed the X-ray diffraction and thermal characteristics of six symmetrical diacid triglycerides involving very short acyl chains—2-acetyldistearin (SC_2S), 2-acetyldipalmitin (PC_2P), 2-butyryldistearin (SC_4S), 2-butyryldipalmitin (PC_4P), 2-caproyldistearin (SC_6S) and 2-caproyldipalmitin (PC_6P). Three of these compounds, PC_2P , SC_4S and PC_4P , have not been discussed previously in the literature, while complete melting points were reported for the others by Grün.⁷

The polymorphism of these six glycerides is unique in many respects. None of them shows a beta prime form. SC_2S and PC_2P show only sub-

alpha-1 and beta-3 forms. SC_4S and PC_4P show three "alpha" forms—sub-alpha-1, alpha-1 and super-alpha-1, and also a beta-3 form. SC_6S and PC_6P show three "beta" forms each—sub-B-beta-3, sub-A-beta-3 and beta-3. SC_6S also shows a clear-cut alpha-1 form transforming from sub-alpha-1; PC_6P shows sub-alpha-3 at low temperatures, but no true alpha form transforming therefrom, perhaps due to the rapid development of beta.

Experimental

The six symmetrical mixed triglycerides were prepared by reacting 1,3-distearin and 1,3-dipalmitin with an excess of the appropriate acid chloride in the presence of pyridine according to established methods. The diglycerides were prepared by directed rearrangement according to the method of Eckey and Formo.⁸ The acetyl and butyryl chlorides were purchased from Eastman Kodak Co. Caproyl chloride was prepared as follows: Starting with carefully purified sorbic acid, successive esterification, hydrogenation, saponification and acidification gave caproic acid which was converted into caproyl chloride by reacting with excess thionyl chloride. The caproyl chloride was distilled before use.

Final purification of the glycerides was accomplished by several (4–6) crystallizations from alcohol-ether followed by thorough drying *in vacuo* over phosphorus pentoxide. Analytical constants for the final products are given in Table I.

TABLE I

	TRIGLYCERIDE ANALYTICAL CONSTANTS						Ref.
	Saponification value		Acid value		M.p., °C.		
	Calcd.	Found	Calcd.	Found	Found	Lit.	
SC_2S	252.3	252.9	0	0.1	62.8	64	7
PC_2P	275.5	276.4	0	0.1	54.8		
SC_4S	242.0	241.4	0	0.3	54.8		
PC_4P	263.4	263.3	0	0.3	46.5		
SC_6S	232.5	233.9	0	<0.3	53.1	47.2	7
PC_6P	252.3	252.1	0	<0.3	44.5	66	7

The polymorphism of the glycerides was studied by X-ray and m.p. techniques described previously.⁵ A General

(8) E. W. Eckey and M. W. Formo, *J. Am. Oil Chem. Soc.*, **26**, 207 (1949).

(1) F. L. Jackson and E. S. Lutton, *This Journal*, **71**, 1976 (1949).

(2) E. S. Lutton, F. L. Jackson and O. T. Quimby, *ibid.*, **70**, 2441 (1948).

(3) E. S. Lutton, *ibid.*, **70**, 248 (1948).

(4) F. L. Jackson and E. S. Lutton, *ibid.*, **73**, 4519 (1950).

(5) T. Malkin and M. L. Meara, *J. Chem. Soc.*, 1141 (1939).

(6) M. G. R. Carter and T. Malkin, *ibid.*, 1518 (1939).

(7) Hefter-Schonfeld, "Chemie und Gewinnung der Fette," Vol. I, 1936.

TABLE II
CHARACTERISTIC THERMAL AND X-RAY DATA

	SC ₂ S	PC ₂ P	SC ₂ S	PC ₂ P	SC ₂ S	PC ₂ P
Melting points, °C.						
Sub-alpha	40.4	28.4	13.4
Alpha	33.4	20.6	27.7	..
Super-alpha	42.7	32.6
Sub-A-beta	46.0	40.5
Sub-B-beta	46.0	40.5
Beta	62.8	54.8	54.8	46.5	53.1	44.5
X-Ray data: long spacings, Å.						
Sub-alpha-1(-3)	28.2 ^a	25.7 ^a	29.8 ^a	26.9 ^a	30.4 ^a	53.7
Alpha-1	28.5 ^a	25.9 ^a	30.0 ^a	..
Super-alpha-1	26.6 ^a	24.2 ^a
Sub-A-beta-3	55.6	52.8
Sub-B-beta-3	54.5	49.2
Beta-3	52.1	47.2	48.4	45.0	56.8	52.5
Short spacings, Å.						
Sub-alpha	4.20 S		4.15 VS		4.20 VS	
	3.78 M		3.71 M		3.70 M	
	2.50 VW					..
Alpha			4.14 S		4.15 VS	..
			2.44 VW		2.50 VW	
			15.75 S			
Super-alpha	5.00 W	
			4.14 VS			
			2.43 VW			
Sub-A-beta		5.15 M
						4.69 S
						4.55 S
						3.86 S+
						3.55 M-
Sub-B-beta		5.38 M
						4.59 VS
						3.87 S
						3.66 S
						5.19 M
Beta	4.59 S		4.60 VS			4.61 VS
	3.87 M		4.04 S			3.82 VS
	3.72 VS		3.85 S			
			3.69 M			
			3.54 M			
Polymorphic stability						
Sub-alpha	Unstable	Unstable	^b	^b	^b	Unstable
Alpha	Unstable	Unstable	Unstable	v. unstable
Super-alpha	Unstable	Unstable
Sub-A-beta	m. stable	Unstable
Sub-B-beta	m. stable	Unstable
Beta	t. stable	t. stable	t. stable	t. stable	t. stable	t. stable

m = moderately, v = very, t = thermodynamically. ^a Single chain length form. ^b Transforms reversibly to alpha.

Electric XRD unit was used to obtain flat film patterns. With a 0.025" pinhole, a sample-to-film distance of 5.0 cm. was employed for most short spacing determinations and 10.0 cm. for detailed short spacing and long spacing data.

Because of the difficulty in distinguishing among and characterizing the beta-like forms of SC₂S and PC₂P, these two glycerides were subjected to detailed microscopic study after the manner of Quimby.⁹ Typically, a flat capillary containing the sample to be examined was placed in a micro-oven which could be heated or cooled and which was provided with a thermocouple for following the temperature. While in the oven, the sample could be observed through the microscope with polarized light and a first order red compensator where applicable. Certain important distinctive appearances of PC₂P forms are shown in Plate A.

Characteristic thermal and X-ray data for the various

polymorphic forms of the six triglycerides are given in Table II.

Discussion

While there is a marked individuality of behavior among the six triglycerides of this paper, there is also a considerable degree of order, particularly a pairing of glycerides which have in common a given shorter acyl chain. Thus, the 2-acetyl glycerides show a high degree of similarity in polymorphic behavior. At higher chain length values (and smaller chain length differences) close similarity between mixed triglycerides in polymorphic behavior is found to occur when chain length differences within the similar glycerides are equal, as

(9) Quimby, THIS JOURNAL, 72, 5064 (1950).

in the pair—2-myristyldipalmitin and 2-palmityl-distearin.¹

The alpha-1 form exhibited by three of the present compounds (SC₄S, PC₄P and SC₆S) has not been reported for other triglycerides. Its long spacing in any given case is much too short for more than a single palmityl or stearyl chain. A postulated "single-chain-length structure" compatible with existing evidence and in keeping with previous interpretation of double- and triple-chain-length spacings is shown in Fig. 1. Somewhat comparable single spacings have been reported for methyl and ethyl esters.¹⁰

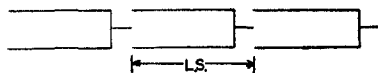


Fig. 1.—Postulated single-chain-length structure.

Sub-alpha forms were obtained for all six triglycerides. Three (SC₄S, PC₄P and SC₆S) were definitely shown to transform reversibly to alpha; the other three were not observed to do so either due to melting below the "transformation point" or because too close approach to the alpha (sub-alpha) m.p. resulted in development of beta. All sub-alpha forms were sub-alpha-1 except the sub-alpha-3 of PC₆P. A form is here interpreted to be of triple chain length when its spacing exceeds that corresponding to two long acyl groups.

Both alpha and sub-alpha forms are obtained by chilling the melt, sub-alpha being obtained at lower temperatures in general.

The super-alpha form, observed for SC₄S and PC₄P, is unique thus far for triglycerides. The name was chosen because the new polymorphic form had the characteristic 4.14 Å. short spacing of alpha while its melting point was 10–12°, higher than that of alpha. Its only other strong "short spacing" occurred at 15.75 Å. which is in the typical long spacing region. The super-alpha form was obtained by tempering the alpha form at 0.5° below its melting point for 2–4 minutes. It was also obtained by growing crystals from the melt (2 to 12 minutes required) at 0.5° above the alpha melting point.

In general, the stable beta-3 forms were readily obtained by solvent-crystallization or transformation of metastable forms.

In order to clarify the polymorphic behavior of the intermediate beta-like forms of SC₆S and PC₆P, thermal and diffraction studies were supplemented by microscopic observations, which proved to be enlightening. Comparable behavior was noted for the two glycerides.

In a typical series of observations, a flat capillary sample of PC₆P was melted and cooled to 12.5° to produce ribbon-like crystals of sub-alpha (see Plate A-(1)). On heating to 13° these crystals melted, and within a few seconds spherulites of negative elongation began to grow. These new crystals were sub-A-beta or sub-B-beta, which were not distinguished microscopically. The number of nuclei and eventual crystal size could be controlled by regulating the temperature. Sub-B-beta, grown

at 17.0° is shown in Plate A-(3). On subsequent rapid heating to 40° momentary melting occurred. Resolidification in a highly disorganized mass of many tiny interlacing needles was observed. This change in appearance is shown in Plate A-(3) and (4). With slower heating, solid phase transformation occurred at 40° to a form (beta) melting at 44.8°. Needles of beta grown directly from melt are shown in Plate A-(2).

After the microscopic observations, it was found that melting phenomena could be observed macroscopically in fine (round) capillaries. By X-ray and m.p. examination of identically pretreated samples, two melting levels could be associated with three beta-like patterns. The upper (and highest) m.p. level was associated with the beta pattern; the lower level was associated with both sub-A-beta and sub-B-beta, which were clearly distinguishable from each other despite their equal m.p.'s. Sub-A-beta was prepared by crystallizing just above the alpha m.p.; sub-B-beta 4–5° higher. "A" was more similar in diffraction pattern to stable beta than was "B," but it also definitely melted below beta and in minor diffraction details was different. While these features seemed strongly indicative of a real distinction between sub-A-beta and beta, the final convincing consideration was the fact that metastable sub-B-beta was obtained at a higher crystallization temperature than "A," both "A" and "B," of course, being convertible to beta. As mentioned previously, the melting of "A" and "B" and resolidification of the melt as beta were clearly observed microscopically. Only after long consideration was the rather complicated nomenclature adopted for the C₆ glycerides. The "sub" designation indicates lower m.p. and the letter signifies more ("A") or less ("B") resemblance of diffraction pattern to that of beta.

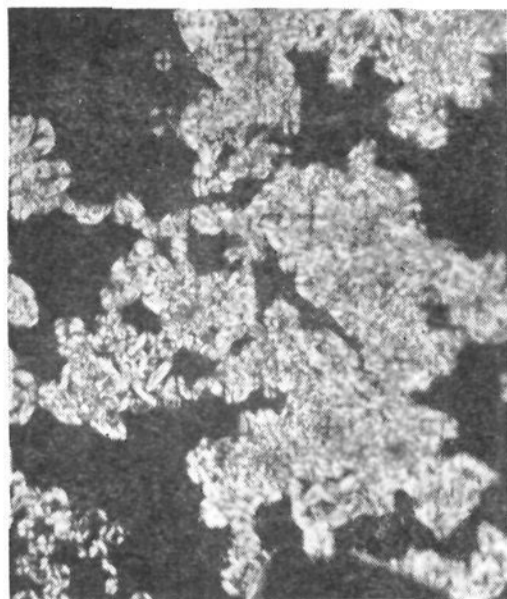
It has not seemed necessary to record complete long spacing data for all forms here reported. Detailed long spacing comparison may be helpful, however, in clarifying certain points, notably the distinctive features of single-chain-length structures and of super-alpha forms. Accordingly, in Table III long spacing data from typical patterns for two forms each of PC₂P and PC₄P are presented. The data of Table III show that single-chain-length forms are characterized by absence of any line corresponding to the strong first order of a triple-chain-length spacing. There is also shown the distinc-

TABLE III
DETAILED LONG SPACING DATA FOR TWO FORMS EACH OF PC₂P AND PC₄P

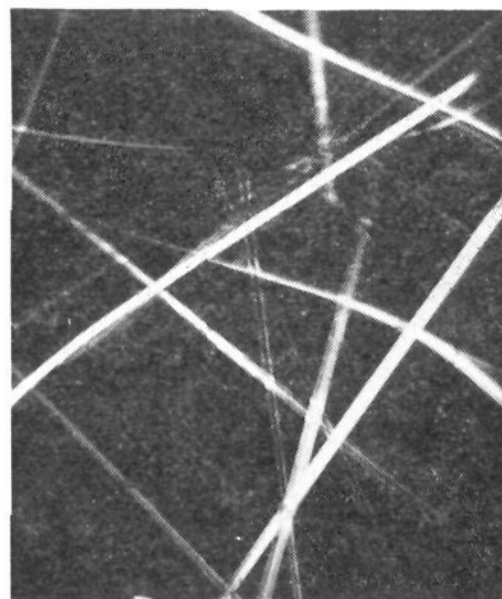
hkl	PC ₂ P				PC ₄ P			
	Sub-alpha-1 d/n	I	Beta-3 d/n	I	Alpha-1 d/n	I	Super-Alpha-1 d/n	I
001	25.2	M	47.6	S	26.0	M	24.4	M
2	12.6	W	23.8	W	12.8	W	12.0	W+
3	8.38	VW	15.9	M	8.70	W-	8.05	W
4			12.0	M				
5								
6			8.00	W+				
7			6.78	VW				
8			5.96	W				
Average d ^a	25.7		47.2		25.9		24.2	

^a Average of all patterns for given form.

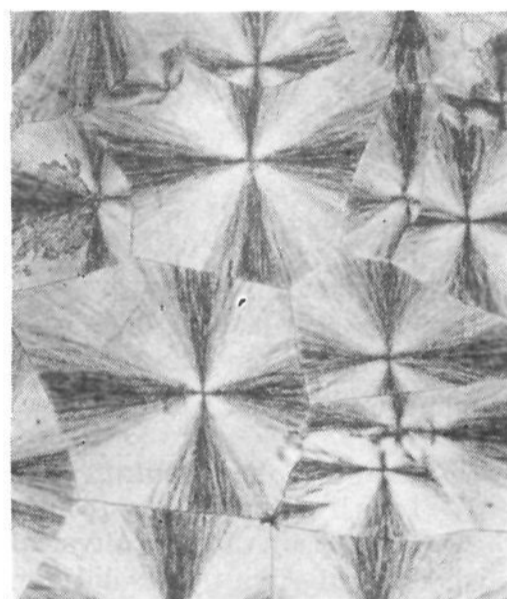
(10) T. Malkin, *J. Chem. Soc.*, 2796 (1931).



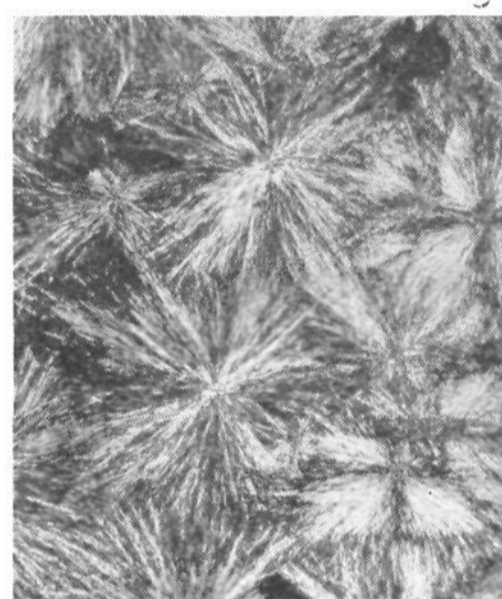
(1) Sub-alpha (alpha) ribbons



(2) Beta-3



(3) Sub-B-beta
From melt at 17.0°.



(4) Beta-3
From sub-B-beta (at left) after heating to 40.2°.

Plate A.—Photomicrographs of PC_eP (130 ×).

tion between alpha-1 and super-alpha-1 and in particular the extraneous 15.7 Å. spacing of super-alpha which seems to be a "short spacing."

SC₂S and PC₂P are the highest melting triglycerides of the six discussed here in spite of their having the lowest molecular weight. PC₆P appears to be the lowest melting glyceride of the entire PC_nP ($n = 2, 4, \dots, 22$) series as shown in Fig. 2 where data are assembled from various sources.^{1,2,4,11,12} Study of the solidification behavior of both SC₈S and PC₈P, near the turning points on the m.p. curves of Fig. 2, would be of interest for clarification of the two homologous series involved.

The low melting behavior of SC₆S and PC₆P is not altogether surprising in view of similar behavior for the normal saturated fatty acids where a m.p. minimum is observed to occur in the region of the four and five carbon acids.¹³

The minima in the m.p. curves of Fig. 2 are evidence that the influence of the polymethylene

chains on solidification tendencies is opposed by forces associated with the very short acyl chains of the present glycerides. It may be that it is the approximate balance of opposing effects which permits

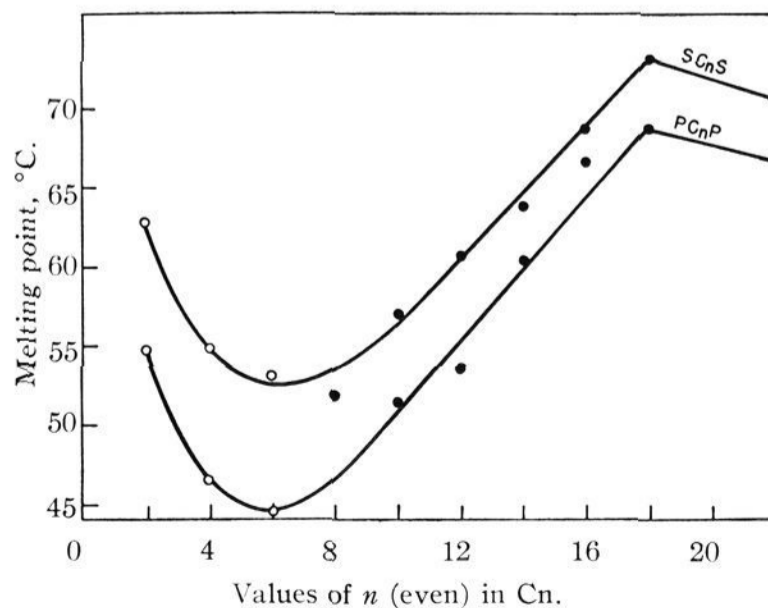


Fig. 2.—M.p.'s of SC_nS and PC_nP triglyceride series: O, present work; ●, literature.

(11) H. E. Robinson, J. N. Roche and C. G. King. THIS JOURNAL, 54, 705 (1932).

(12) T. Malkin and M. L. Meara. J. Chem. Soc., 1141 (1939).

(13) A. E. Bailey, "Melting and Solidification of Fats," Interscience Publishers, Inc., New York, N. Y., 1950, p. 147.

the multiplicity of structure types encountered here.

Acknowledgment.—The authors are indebted to Mr. R. G. Folzenlogen for the syntheses of

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CINCINNATI 17, OHIO

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Synthesis of Unsymmetrical α -Ketols by the Mixed Acyloin Reaction

BY JOHN W. LYNN¹ AND JAMES ENGLISH, JR.

The conditions for optimum yield in a mixed acyloin reaction have been determined for ethyl benzoate and ethyl propionate. The reaction has been extended to several analogous esters and consideration given to the problem of chain-extension by use of this reaction.

A survey of the literature concerning the acyloin reaction² revealed only limited application to the synthesis of unsymmetrical α -ketols. Other reported methods for the preparation of compounds of this class frequently suffer from the disadvantage of requiring relatively inaccessible starting materials.³⁻⁸ The mixed acyloin reaction has previously been employed only by Baudart⁹ in his synthesis of several unsaturated long-chain fatty acids and by Kapron¹⁰ who used the analogous bimolecular reduction of an ester-ketone mixture.

In the present work a model pair of esters, ethyl benzoate and ethyl propionate was employed, and a study made of the effect of varying the solvent, reaction time, and concentration of each reactant. The mixed coupling products isolated from the reaction were phenylpropionylcarbinol, 1-phenylbutanedione-1,2 and 1-phenylbutanediol-1,2. Benzoin and propionin were also obtained, the yields being quite small in comparison with the yield of mixed coupling product. The remainder of the material could be accounted for as an acidic fraction and polymeric residue from the distillation. A summary of the results of this study is given in Table I. The yields given represent fractions isolated by distillation from the hydrolyzed reaction mixture. The fractions consisted mainly of the component indicated, as was shown by preparation of solid derivatives. The difficulty of making a clean separation of acyloin products has been noted previously.¹¹ Since the products are readily interconvertible the success of synthetic application of the reaction would depend upon the total yield of mixed coupling product.

Phenylpropionylcarbinol was synthesized independently by the reaction of ethylmagnesium bromide with mandelamide.² Oxidation and reduction of this compound gave, respectively, 1-phenyl-

TABLE I
VARIATION OF REACTION CONDITIONS^a

Variable	α -Ketol, %	α -Di- ketone, %	α -Glycol, %
Benzene solvent	16	1	1
Ether solvent	10	5	
Xylene solvent	7.5	6	
Reaction time, 2 hours	7.5	8.5	
Reaction time, 4 hours	16	1	1
Reaction time, 8 hours	9.5	3.5	3.0
Calculated reactant ratio	16	1	1
100% excess sodium	3	3.0	5.0
100% excess ethyl benzoate	12		8.0
100% excess ethyl propionate	23.0		10
200% excess ethyl propionate	22.0		

^a Reaction times were 3-4 hours except where indicated.

butanedione-1,2 and 1-phenylbutanediol-1,2, shown to be identical with the products from the acyloin reaction by a comparison of their physical constants and by mixed melting points of solid derivatives.

Since benzene proved to be the best of the usable solvents it was used exclusively in later experiments. The duration of reaction period appears to affect only the ratio of α -ketol, α -diketone and α -glycol obtained. It is logical to expect a short reaction time to favor the formation of a greater percentage of α -diketone since it has been shown that diketones are the primary reaction products which are subsequently reduced to the α -ketols^{11,12} and α -glycols.

Assuming that the mechanism proposed by Blicke¹³ and Kharasch¹² is correct, the calculated proportion of reactants required to form the α -ketol is two moles of sodium per mole of ester mixture. It is apparent that an excess of sodium adversely affects the percentage of mixed-coupling product obtained; an excess of ethyl propionate, however, causes a striking increase in yield. This marked increase in yield may be accounted for by the fact that the metal ketyl produced by the reaction of sodium and ethyl propionate would be expected to possess a much greater reactivity than the ketyl from ethyl benzoate, since the latter may exist as a relatively stable resonance hybrid.^{14,15}

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