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cule. In the activated complex of the reaction the amino group and the halide atom are most probably both weakly bound to the carbon on which the substitution takes place. During the formation of this complex the negatively charged NH<sub>2</sub> group must therefore approach this carbon. A positive charge on the carbon will naturally speed up the reaction by lowering the energy necessary for the formation of the activated state. With two compounds in which all factors but this are the same one will therefore expect the one with the greater positive charge on the reacting carbon to have the greater reaction velocity. The halogen atoms in the C-Cl and C-Br linkages are negative with respect to the carbon. The presence of this small positive charge on the carbon is shown by the dipole moments of compounds like methyl bromide and methyl chloride. When there is a side chain linked to this carbon, some of the charge is induced down the chain through the covalent bonds. This lowers the charge on the carbon atom which is linked to the halogen atom and slows the reaction. The nearer a carbon atom is to the one which carries the initial charge, the more of the charge it acquires. Therefore, a branched chain will slow the reaction more than a normal side chain of the same length.

The results described in the first parts of this paper as well as those of Abderhalden<sup>6b,c</sup> agree with this picture of the reaction mechanism. The rates of reaction for the normal  $\alpha$ -bromo aliphatic acids decrease with increasing size of the acid

molecule. The drop between the rates of bromoacetic and  $\alpha$ -bromopropionic acids is large but the effect is smaller as one goes further in the series. Abderhalden's results show that, with the branched chain compounds, the effect is greater the nearer the branching is to the  $\alpha$ -carbon. Thus the rates of ammonolysis of the various caproic acids decrease in the order:  $\alpha$ -bromo-*n*caproic acid >  $\alpha$ -bromo-4-methylvaleric acid >  $\alpha$ -bromo-3-methylvaleric acid. The effect of changing the free carboxyl into a peptide linkage is not definite from this work. Chloroacetylglycine reacts faster than chloroacetic acid, while  $\alpha$ -bromoisocaproylglycine reacts slower than the corresponding acid.

### Summary

The rates of reaction of nine different  $\alpha$ -halogen acids and  $\alpha$ -halogen acyl peptides with an excess of ammonia have been measured and the first order constants determined.

The reactions have been shown to be bimolecular because the first order constants are proportional to the partial pressures of ammonia in equilibrium with the solutions.

The heats and entropies of activation have been calculated for the reactions starting with gaseous ammonia at one atmosphere.

By means of the measurements the yields obtained from the ammonolysis reaction have been increased.

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# A New Method for the Esterification of Certain Sterically Hindered Acids

# BY MELVIN S. NEWMAN

The fact that certain substituted benzoic acids are not appreciably esterified on refluxing with alcohols containing mineral acids has long been known. The method most commonly used for preparing methyl esters of such sterically hindered acids consists in treating the acid with diazomethane. Other methods involve treatment of the acid chloride with methanol, heating of the silver salt with methyl iodide, and pyrolysis of the tetramethylammonium salt.<sup>1</sup> With the exception of alcoholysis of the acid chloride all of

(1) Fuson, Corse and Horning, This JOURNAL, 61, 1290 (1939).

these methods have obvious disadvantages if other than methyl esters are to be prepared. In this paper a new method for the esterification of certain sterically hindered acids is described. This method consists in dissolving the acid to be esterified in approximately 100% sulfuric acid and pouring the solution into the desired alcohol. In principle the new procedure is not limited with respect to the alcohol although we have been unable to prepare an ester from *t*-butyl alcohol in this way. The following esters have been prepared in excellent yield by this method: methyl, ethyl,

<sup>[</sup>CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

and isopropyl 2,4,6-trimethylbenzoates; methyl 2,4,6-triethylbenzoate<sup>2</sup>; and methyl 2,4,6-triisopropylbenzoate.<sup>2</sup> In addition, by dissolving each of these esters in 100% sulfuric acid and pouring into water, the corresponding acids were recovered in over 90% yields. A notable feature of this method is the short time needed for esterification, for only a few minutes are required. It is also noteworthy that benzoic acid is not esterified to any great extent by this procedure.

In order to explain why this particular procedure was adopted and why-it is so effective, it is necessary to review certain properties of solutions of organic compounds in solvent sulfuric acid. As so clearly demonstrated by Hammett and coworkers,<sup>3</sup> sulfuric acid is an excellent solvent for studying the basic ionization (in the Brönsted sense) of organic molecules. Measurement of the freezing point of various solutions has shown that many organic substances ionize almost completely (have van't Hoff *i* factors of nearly two<sup>4</sup>) as monoacid bases according to the following equation

$$B + H_2SO_4 \implies BH^+ + HSO_4^-$$
(1)

Examples of this type of substance are acetic acid, benzoic acid, several substituted benzoic acids and several esters. 2,4,6-Trimethylbenzoic acid proved to be an interesting exception for it was shown to have a van't Hoff *i* factor of almost four.<sup>5</sup> According to Hammett the *i* factor of four is explained by the following equation

 $(CH_3)_8C_6H_2COOH + 2H_2SO_4 \swarrow$   $(CH_3)_8C_6H_2CO^+ + H_3O^+ + 2HSO_4^- (2)$ 

In itself this behavior would not have been so suggestive were it not for the additional observation that methyl 2,4,6-trimethylbenzoate was hydrolyzed completely by dissolving in concentrated sulfuric acid and pouring into water, whereas methyl benzoate was recovered unchanged after similar treatment.<sup>5</sup> These facts suggested that in all probability methyl 2,4,6-trimethylbenzoate has an *i* factor of four and methyl benzoate an *i* factor of two. The behavior of these esters in sulfuric acid may be represented by the equations

(4) The van't Hoff i factor gives the ratio of the freezing point depression observed to the freezing point depression which would have resulted if no dissociation had occurred.

$$C_{6}H_{5}COOCH_{3} + H_{2}SO_{4} \swarrow C_{6}H_{5}CO_{2}CH_{3}\cdot H^{+} + HSO_{4}^{-} (3)$$

$$(CH_{3})_{3}C_{6}H_{2}COOCH_{3} + 2H_{2}SO_{4} \swarrow (CH_{3})_{3}C_{6}H_{2}CO^{+} + CH_{3}OH_{2}^{+} + 2HSO_{4}^{-} (4)$$

Treatment with water produces the following results

$$C_{6}H_{5}CO_{2}CH_{8}\cdot H^{+} + H_{2}O \xrightarrow{} C_{6}H_{5}COOCH_{3} + H_{8}O^{+} \quad (5)$$

$$(CH_{8})_{3}C_{6}H_{2}CO^{+} + H_{2}O \xrightarrow{} (CH_{3})_{5}C_{6}H_{2}COOH + H^{+} \quad (6)$$

Consideration of the above facts and hypotheses led the author to believe that if a sulfuric acid solution containing a positive acyl ion, such as  $(CH_3)_3C_6H_2CO^+$ , were added to an alcohol the corresponding ester would be produced. This prediction finds its fulfillment in the esterification method herein described. The final step may be formulated as follows

 $(CH_s)_{3}C_{6}H_{2}CO^{+} + ROH \Longrightarrow$ 

 $(CH_3)_3C_6H_2COOR + H^+$  (7)

Two more experiments were performed to add to the qualitative evidence advanced in support of the above mechanisms. Quantities of 2,4,6trimethylbenzoic acid were dissolved in 96% sulfuric acid and in 100% sulfuric acid containing dissolved potassium bisulfate. On pouring these solutions into absolute methanol the degree of esterification was considerably less than in the case where 100% sulfuric acid alone was used. When one considers that in both of these cases the concentration of bisulfate ions in the sulfuric acid used was higher than in 100% sulfuric acid, the results are those to be expected by application of the law of mass action to the ionization phenomena in question.

It should be emphasized that only those acids which readily yield a positive acyl ion in sulfuric acid will be esterified by this method. The ionizations as represented in equations (2) and (7) are rapid reactions and the processes taking place in the new esterification method should not be confused with the ordinary acid-catalyzed esterification which generally proceeds at a much slower rate. Furthermore, it does not necessarily follow that all sterically hindered acids will, or all unhindered acids will not, be esterified by the new method. Specifically, the sterically hindered 2,4,6tribromobenzoic acid is not esterified while the unhindered *o*-benzoylbenzoic acid is.

Theoretical Discussion Concerning the Ionization of Organic Molecules in Sulfuric Acid.— The general topic of basic ionization of organic

<sup>(2)</sup> Samples of these two acids were provided through the courtesy of Professor R. C. Fuson of the University of Illinois.

<sup>(3)</sup> For an excellent account of the behavior of sulfuric acid and its solutions see Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 45 to 49 and 278 to 281.

<sup>(5)</sup> Hammett and Treffers, THIS JOURNAL, 59, 1708 (1937).

molecules in solvent sulfuric acid has been treated quite thoroughly by Hammett.<sup>3</sup> However, further consideration of this field permits the grouping of certain processes in a more general manner. It is with these generalizations that this discussion is mainly concerned.

If one compares equations (1) (where B is benzoic acid) and (2), it would appear that there is a sharp distinction between the ionization of benzoic acid and 2,4,6-trimethylbenzoic acid. Since these two acids should have the same basicity (as judged by the fact that they have approximately the same ionization constants in water) one would not expect such widely different behavior in sulfuric acid.<sup>6</sup> From the standpoint of a more general theory it seems more desirable to consider that all carboxylic acids are involved in the following equilibria in concentrated sulfuric acid solutions

$$\begin{array}{c} \text{RCOOH} + \text{H}_2\text{SO}_4 &\longrightarrow \text{RCO}_2\text{H}_2^+ + \text{HSO}_4^- & (8) \\ \text{RCO}_2\text{H}_2^+ &\longleftarrow \text{RCO}^+ + \text{H}_2\text{O} & (9) \\ \text{H}_2\text{O} + \text{H}_2\text{SO}_4 &\longleftarrow \text{H}_3\text{O}^+ + \text{HSO}_4^- & (10) \end{array}$$

The first step in the basic ionization of all acids in sulfuric acid may thus be represented by the same equation. This equation relates to the distribution of a proton between the weak base,  $HSO_4^-$ , and the stronger base, RCOOH. The stronger RCOOH is as an acid in water, the weaker it will be as a base and the less the tendency for the equilibrium represented in equation 8 to proceed to the right. The failure of 2,4,6-tribromobenzoic acid to be esterified by the new method may be because of an unfavorable equilibrium in equation (8), for it is a much stronger acid (K = $3.8 \times 10^{-2}$ ) than methyl substituted benzoic acids.

The decomposition of the conjugate acid,  $RCO_2H_2^+$ , into a positive acyl ion and water (equation (9)) represents a reaction which ordinarily does not proceed to an appreciable extent in 100% sulfuric acid as judged by the usual *i* factors of two. With certain acids, however, the conjugate acid is unstable and the equilibrium represented in equation (9) lies far to the right. The ionization of the water formed likewise lies far to the right, and a summation of equations (8), (9) and (10) yields equation (2).

A consideration of the equilibrium represented

(6) Hammett, ref. 5, p. 1712, also appreciated this argument and advanced the following equations to account for the behavior of acids having a van't Hoff *i* factor of four

 $RCOOH + H_2SO_4 \longrightarrow RCO_2H_2^+ + HSO_4^-$ 

$$RCO_2H_2^+ + H_2SO_4 \longrightarrow RCO^+ + H_3O^+ + HSO_4^-$$

by equation (9) is of considerable theoretical interest. In seeking to account for the ease with which the conjugate acid,  $(CH_3)_3C_6H_2CO_2H_2^+$ , expels water whereas the conjugate acids of other substituted benzoic acids which have been examined cryoscopically<sup>5</sup> fail to do so, two factors may be mentioned. It seems fairly well established that a methyl group on a benzene ring tends to build up a negative charge in positions ortho and para to the methyl group. The 2,4,6-trimethylphenyl group would be expected to show this effect to a maximum degree, for only when the methyl groups are meta to each other do they reinforce each other in building up a negative charge. The negative charge on the carbon attached to the carbonyl carbon carrying the positive charge of the positive acyl ion would tend to increase the stability of the ion, I, and hence tend to drive the equilibrium of equation (9) to the right.



Evidence is available, however, which indicates that this is not the only effect. The negative charge built up would be expected to be approximately the same for 2,4-dimethylbenzoic acid and 2,6-dimethylbenzoic acid. Yet freezing point experiments<sup>5</sup> show that the 2,4-acid has a van't Hoff *i* factor of two whereas the 2,6-acid has an *i* factor of over three, indicating dissociation of the conjugate acid according to equation (9). A steric factor must then be considered. The following explanation is offered.

For the conjugate acid,  $(CH_3)_3C_6H_2CO_2H_2^+$ , three resonating structures in which there is a double bond between the carbon of the carboxyl group and the ring carbon may be written, as shown below.



This double bond requires that the oxygen atoms (at least) of the hydroxyl groups lie in the same plane as the ring and the methyl groups. With the aid of atom models<sup>7</sup> it appears likely that owing to spatial relationships there is a repulsion between hydroxyl and methyl groups. This repulsion would be expected to increase the tendency to split out water, especially since, as indicated above, the positive ion, I, produced is one whose stability is favored by the location of the methyl groups on the benzene ring.<sup>8</sup>

In connection with the resonance effect above mentioned, it is significant that triphenylcarbinol has a van't Hoff *i* factor of four in sulfuric acid<sup>9</sup> whereas other alcohols have an *i* factor of three. The ionization of these alcohols is represented in the following manner according to Hantzsch and Hammett

$$(C_{6}H_{\delta})_{3}COH + 2H_{2}SO_{4} \xleftarrow{} (C_{6}H_{\delta})_{3}C^{+} + H_{3}O^{+} + 2HSO_{4}^{-} (11)$$
  
ROH + 2H\_{2}SO\_{4} \xleftarrow{} ROSO\_{2}OH + H\_{3}O^{+} + HSO\_{4}^{-} (12)

Here too its seems advantageous to consider the following mechanism of ionization for all alcohols in sulfuric acid

$$\operatorname{ROH} + \operatorname{H}_2\operatorname{SO}_4 \longrightarrow \operatorname{ROH}_2^+ + \operatorname{HSO}_4^- \quad (13)$$

$$H_{10} + H_{10} + H$$

$$R^+ + HSO_4^- \implies ROSO_2OH$$
 (16)<sup>10</sup>

The summation of these last four equations yields equation (12), and this represents the behavior of most alcohols in sulfuric acid. In the case of triphenylcarbinol, however, we may assume that the positive ion,  $R^+$ , is stabilized by resonance effects and reaction (16) does not occur to an appreciable extent. Summation of equations (13), (14) and (15) then yields equation (11).

In conclusion, the author would like to express his appreciation to Professor E. N. Lassettre for valuable advice and criticism in the preparation of this manuscript.

#### Experimental<sup>11</sup>

The 100% sulfuric acid used in this work melted in the range 9–10° and was prepared by suitable mixing of 96% acid and 20% oleum. Approximately equal weights of these two acids are required.

Preparation of Esters .--- Since all esterification experiments were carried out in essentially the same way a typical experiment will be described. About 2 g. of acid to be esterified was dissolved in from 14 to 20 cc. of 100%sulfuric acid. After standing at room temperature for a few minutes, this solution was poured into an excess of a cold absolute alcohol contained in a Claisen flask. When most of the alcohol had been removed under reduced pressure, about 50 cc. of water was added and more alcohol removed under reduced pressure. The organic matter was taken into ether and treated with sodium carbonate solution. The unesterified acid was recovered from the alkaline extracts by acidification and filtration and was weighed and identified by mixed melting point determination. The ester formed was distilled from a small, specially constructed Claisen flask and identified by analysis and by hydrolysis to the corresponding acid as described below. The yields, properties and analysis of each ester are reported below. It should be pointed out that the yields reported refer to the pure distilled esters. A better measure of the total ester formed is obtained by subtracting the per cent. of recovered acid from 100%.

Methyl 2,4,6-Trimethylbenzoate.—Obtained in 78% yield (9% acid recovered) as a colorless liquid; b. p.  $114.8-115.2^{\circ}$  (7.0-7.5 mm.),  $n^{20}$ p 1.5083.

Anal. Calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>: C, 74.1; H, 7.9. Found: C, 74.1, 74.7; H, 7.8, 8.1.

In comparable experiments using 1.00 and 2.00 g. of 2,4,6-trimethylbenzoic acid in 10 cc. of 96% sulfuric acid and 14 cc. of 100% sulfuric acid containing 3.4 g. of potassium acid sulfate there was obtained 0.36 g. (36%) and 0.58 g. (29%), respectively, of 2,4,6-trimethylbenzoic acid. The remaining product was ester but was not worked up quantitatively.

Methyl 2,4,6-Triethylbenzoate.—Obtained in 80% yield (9% acid recovered) as a colorless liquid; b. p. 93.2-93.8° (0.5-1.0 mm.),  $n^{20}$ p 1.5016.

Anal. Calcd. for  $C_{14}H_{20}O_2$ : C, 76.3; H, 9.2. Found: C, 76.4, 76.1; H, 9.6, 9.7.

Methyl 2,4,6-Triisopropylbenzoate.—Obtained in 81% yield (7.5% acid recovered) as a colorless solid; m. p.  $37.0-38.4^{\circ}$ , b. p.  $99.6-100.4^{\circ}$  (0.5-1.0 mm.),  $n^{20}$ D 1.4931 (before it crystallized).

Anal. Calcd. for C<sub>17</sub>H<sub>28</sub>O<sub>2</sub>: C, 77.8; H, 10.0. Found: C, 77.8, 77.1; H, 10.2, 10.0.

Ethyl 2,4,6-Trimethylbenzoate.—Obtained in 66% yield (17% acid recovered) as a colorless liquid; b. p.  $115.0^{\circ}$  (6.0–6.5 mm.),  $n^{20}$ D 1.5014.

Anal. Calcd. for  $C_{12}H_{10}O_2$ : C, 75.0; H, 8.4. Found: C, 74.8, 74.9; H, 8.2, 8.2.

Isopropyl 2,4,6-Trimethylbenzoate.—Obtained in 59% yield (19% acid recovered) as a colorless liquid; b. p.  $120.2-121.0^{\circ}$  (6.0-6.5 mm.),  $n^{20}$ D 1.4940.

Anal. Calcd. for  $C_{13}H_{18}O_2$ : C, 75.7; H, 8.8. Found: C, 75.7, 75.6; H, 8.7, 8.7.

Hydrolysis of Esters.—A portion of each of the esters above mentioned was dissolved in 100% sulfuric acid. After a few minutes this solution was poured on ice and the acid thus produced separated, washed, dried, and weighed. It was possible to account for over 90% of the theoretical

<sup>(7)</sup> Fisher-Hirschfelder models built to scale.

<sup>(8)</sup> A discussion of factors which are involved in the formation of acyl ions is also given by Hammett and Treffers, ref. 5, p. 1712.

<sup>(9)</sup> Hantzsch, Z. physik. Chem., 61, 257 (1908); see also Hammett and Deyrup, THIS JOURNAL, 55, 1900 (1933).

<sup>(10)</sup> There are also several other possibilities of reaction of the positive ion,  $\mathbb{R}^+$ , as pointed out by Whitmore, *ibid.*, **54**, 3274 (1932), and by others.

<sup>(11)</sup> Analyses by The Arlington Laboratories, Chagrin Falls, Ohio.

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amount as corresponding acid. The acids were identified by mixed melting point determinations.

#### Summary

A new method for the esterification of certain sterically hindered acids is described. This method consists in pouring a 100% sulfuric acid solution of the acid to be esterified into the desired alcohol.

Theoretical considerations concerning the behavior of organic substances in sulfuric acid are discussed.

COLUMBUS, OHIO

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[Contribution from the College of Pharmacy, University of Michigan]

# 1-Dialkylaminoalkyl 2-Alkyl 3-Aminophthalates as Local Anesthetics

By F. F. Blicke and Chieko Otsuki<sup>1</sup>

Recently we described a series of 1-alkyl 2dialkylaminoalkyl 3-aminophthalates<sup>2</sup> and reported that a number of them are strong local anesthetics.

This paper deals with the preparation of 1-dialkylaminoalkyl 2-alkyl 3-aminophthalates which were obtained by a series of simple reactions: conversion of 3-nitrophthalic anhydride into a 2alkyl 3-nitroacidphthalate by means of an alkanol; treatment of the monoester with a dialkylaminoalkyl chloride whereupon a 1-dialkylaminoalkyl 2-alkyl 3-nitrophthalate hydrochloride was formed; reduction of the nitro group in the diester with stannous chloride and hydrogen chloride in acetic acid solution.

Many of the products were found to be more active than cocaine when tested on the rabbit cornea; the salts of 1- $(\beta$ -diethylaminoethyl) 2amyl and 1- $(\beta$ -diethylaminoethyl) 2-hexyl 3aminophthalate are especially strong local anesthetics. A detailed pharmacological report will be published later by L. W. Rowe, who examined the esters in the Parke, Davis and Company Laboratories.

## Experimental

2-Alkyl 3-Nitroacidphthalates.<sup>2</sup>—A mixture of 0.25 mole of 3-nitrophthalic anhydride<sup>4</sup> and 1.25 moles of the required alcohol was heated on a steam-bath for five hours, the excess alcohol removed by distillation under reduced pressure and the residue treated with 10% sodium carbonate solution. The mixture was filtered, the filtrate acidified, the precipitated monoester filtered and recrystallized from a suitable solvent—water, alcohol, dilute alcohol or benzene. In order to obtain the monolauryl and the monostearyl esters, the nitro anhydride was heated in xylene solution with 1:1 molecular quantity of the alcohol for six hours at  $145-150^{\circ}$ .

The esters must be highly purified before use.

1-( $\beta$ -Diethylaminoethyl) 2-Alkyl 3-Nitrophthalate Hydrochloride.—A mixture of 0.05 mole of 2-alkyl 3-nitroacidphthalate. 0.45 mole of  $\beta$ -diethylaminoethyl chloride<sup>5</sup> and 30 cc. of dry *iso*propyl alcohol<sup>5</sup> was heated on a steambath for five hours and the solvent removed by distillation under reduced pressure. The crude hydrochloride was purified by recrystallization.

The 3-amino esters were obtained in the manner described previously.<sup>7</sup>

Several cases were noticed in which the hydrochlorides of the isomeric esters possessed identical or very similar melting points: thus, both 1-ethyl 2-( $\beta$ -diethylaminoethyl) 3-nitrophthalate hydrochloride and 1-( $\beta$ -diethylaminoethyl) 2-ethyl 3-nitrophthalate hydrochloride melt at 126–128°; however, the mixed melting point was found to be 114–124°.

In a few instances in which the hydrochloride of the nitro or the amino ester could not be obtained in crystalline form, the hydrobromide, citrate or methiodide<sup>2</sup> was prepared.

 $\gamma$ -Dibutylaminopropyl chloride hydrochloride was obtained when a mixture of 18.7 g. of  $\gamma$ -dibutylaminopropyl alcohol, 75 cc. of chloroform and 25 cc. of thionyl chloride was heated for two hours on a steam-bath and the solvent and excess thionyl chloride removed under diminished pressure. The crude salt was dissolved in water, the basic chloride liberated with sodium bicarbonate, the product extracted with ether, the solution dried and the solvent removed. The material was used immediately.

The chloroaurate, obtained as yellow needles after recrystallization from dilute alcohol, melted at 143–146  $^\circ.$ 

Anal. Calcd. for  $C_{11}H_{25}NCl_5Au$ : Au, 36.13. Found: Au, 36.06.

The preparation of  $\gamma$ -dimethylamino  $\beta$ , $\beta$ -dimethylpropyl chloride hydrobromide has been published<sup>2</sup> and  $\gamma$ -piperidinopropyl bromide hydrobromide will be described later.

<sup>(1)</sup> This paper represents part of a dissertation submitted to the Horace H. Rackham School of Graduate Studies by Chieko Otsuki in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

<sup>(2)</sup> Blicke and Otsuki, THIS JOURNAL, 63, 1945 (1941).

<sup>(3)</sup> A long series of these esters has been described by Dickinson, Crosson and Copenhaver, *ibid.*, **59**, 1094 (1937).

<sup>(4) &</sup>quot;Organic Syntheses," Coll. Vol. I, p. 402.

<sup>(5)</sup> Slotta and Behnisch, Ber., 68, 758 (1935).

<sup>(6)</sup> In the case of 2-lauryl and the 2-stearyl esters, xylene was used as a solvent and the mixture was heated for five hours at  $120-130^{\circ}$ .

<sup>(7)</sup> Blicke and Parke, THIS JOURNAL, 61, 1201 (1939).