[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Reaction of Various Alkyl Benzoates with Sodium Alkoxides

BY ARTHUR MAGNANI[1] AND S. M. MCELVAIN

Among the numerous types of compounds that are produced by the action of sodium alkoxides on esters, the two the formation of which seems most difficult to understand are the sodium salt of the acid, $RCOONa$, and the diacylmethane, $(RCO)_2CH_2$, corresponding, respectively, to the acid and acyl group of the ester. Suggestions as to the origin of the sodium salt have appeared in the literature. Adickes[2] pointed out that the material which Claisen[3] thought to be an addition product of ethyl benzoate and sodium ethoxide was really a mixture of sodium benzoate and the alkoxide, and suggested that the sodium benzoate might be formed through saponification of the ester by traces of moisture. Scheibler[4] later explained the relatively large amounts of sodium benzoate which he obtained from the reaction of ethyl benzoate with sodium ethoxide by the reaction

$$C_6H_5COOC_2H_5 + C_2H_5ONa \longrightarrow C_6H_5COONa + C_2H_4 + C_2H_5OH$$

The experimental evidence for this proposal was the isolation of ethylene bromide when the gas, obtained by heating the ester and alkoxide at 160°, was passed through bromine. Adickes,[5] however, demonstrated that Scheibler's proposal was untenable because the gas evolved from this reaction mixture contained only small amounts of ethylene, but consisted mainly (95%) of carbon monoxide. The relatively large amount of sodium benzoate which was produced in the reaction could not be accounted for by the small amount of ethylene present in the gaseous reaction products. Adickes pointed out that the water necessary for the saponification of the ester might be derived from condensations taking place in the reaction mixture.

From the reaction of ethyl benzoate with sodium ethoxide, Adickes reported[5] the isolation of dibenzoylmethane in yields of approximately 20% of the theoretical. This same type of reaction product, *i. e.*, difuroylmethane, had been obtained in this Laboratory during a study of the condensation of ethyl furoate with ethyl acetate by means of sodium ethoxide.[6] Further experimentation to trace the origin of this unexpected substance showed that it could be formed in yields of 10% of the theoretical by simply heating ethyl furoate with sodium ethoxide on a steam-bath for two days. Later, dibenzoylmethane was obtained as the main reaction product from an attempted condensation of ethyl benzoate with α-picoline by means of sodium ethoxide.[7]

Adickes suggested that the formation of dibenzoylmethane from ethyl benzoate might be due to the elimination of formaldehyde from the ester followed by the condensation of the resulting acetophenone with the ester to form the diketone

$$C_6H_5COOCH_2CH_3 \longrightarrow C_6H_5COCH_3 + CH_2O$$

$$C_6H_5COCH_3 + C_6H_5COOC_2H_5 \xrightarrow{NaOC_2H_5} (C_6H_5CO)_2CH_2 + C_2H_5OH$$

He paralleled the formation of carbon monoxide from the reaction of ethyl benzoate with sodium ethoxide to the decomposition of formate esters

$$HCOOC_2H_5 \longrightarrow CO + C_2H_5OH$$

$$C_6H_5COOC_2H_5 \longrightarrow CO + C_6H_5OC_2H_5$$

However, he did not report the isolation of any phenetole from the reaction of ethyl benzoate with sodium ethoxide.

In addition to the reaction of ethyl benzoate with sodium ethoxide, Adickes[5] also had studied the reaction of methyl and *n*-propyl benzoates with the corresponding alkoxides. In the case of methyl benzoate, he reported dimethyl ether and sodium benzoate as the main reaction products. These compounds had formed by a type of Williamson reaction

$$C_6H_5COOCH_3 + NaOCH_3 \longrightarrow C_6H_5COONa + CH_3OCH_3 \quad (1)$$

A yield of the ether of approximately 55% of the theoretical was obtained. From the reaction of *n*-propyl benzoate with sodium *n*-propoxide Adickes identified sodium benzoate, carbon monoxide and propiophenone, but in addition to these compounds he obtained material of wide boiling range which could not be successfully fractionated. Only in the case of ethyl benzoate was he able to isolate any of the 1,3-diketone.

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(1) Wisconsin Alumni Research Foundation Scholar and Fellow, 1934–1937.

(2) Adickes, *Ber.*, **58**, 1994 (1925).

(3) Claisen, *ibid.*, **20**, 653 (1887).

(4) Scheibler, *ibid.*, **65**, 998 (1932).

(5) Adickes, *ibid.*, **66**, 1904 (1933).

(6) R. J. Baird, University of Wisconsin M.S. Thesis, 1933.

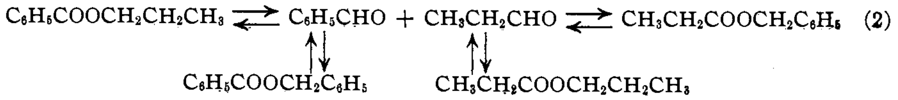
(7) P. S. Pinkney, University of Wisconsin B.S. Thesis, 1934.

It seemed that more light might be shed on the mechanism of the diketone formation, and possibly also upon the formation of sodium benzoate, from a study of the reaction of various alkyl benzoates with the corresponding sodium alkoxides. This paper reports the results of such a study. As a beginning, Adickes' work with ethyl benzoate was repeated under varying conditions in order to find those conditions that produced a maximum yield of the diketone. From this work it appeared that a ratio of 4 moles of the ester to 1 mole of the alkoxide, at a temperature of 175–180° for two hours, produced a maximum yield (40%) of dibenzoylmethane (I). This temperature and ratio of reactants then were used with the other alkyl benzoates that were studied. With this amount of ester in the reaction a considerable quantity of unchanged ester was always recovered.

Experiments with methyl and ethyl benzoates yielded the same reaction products as were reported by Adickes. However, an additional compound, benzyl benzoate, was obtained from the reaction of each of these esters with the alkoxide. In the case of methyl benzoate the amount of the benzyl ester was quite small, since the main reaction products were dimethyl ether and sodium benzoate. With ethyl benzoate, however, the yield of benzyl benzoate amounted to 0.15 mole from 2.1 moles of reacting ester.

n-Propyl benzoate with sodium *n*-propoxide was found to yield a much larger variety of products than did the ethyl ester. By careful and repeated fractional distillation it was possible to isolate from the reaction products of the *n*-propyl ester, benzyl benzoate, propiophenone (III), 2-methyl-1-pentanol (IV) and its benzoate, ethylphenylcarbinol (II) and its benzoate, carbon monoxide, along with benzoic acid and *n*-propyl alcohol. The amounts of these higher alcohols, 2-methyl-1-pentanol and ethylphenylcarbinol were, as may be seen from Table I, quite substantial. No evidence of a 1,3-diketone could be obtained with this ester.

The fact that benzyl benzoate is a common product of the reaction of the above three alkyl benzoates suggests that these reactions, although apparently quite different, may follow a common initial course. This common course appears to be a reverse Tischtschenko reaction produced catalytically by the action of the sodium alkoxide on the alkyl benzoate. The resulting aldehydes are then available for further reaction, and since the sodium alkoxides are not specific catalysts a number of different types of reaction may be expected. For example, forward Tischtschenko reactions could produce three new esters in addition to the starting ester. To illustrate with *n*-propyl benzoate



$$\begin{tikzcd} C_6H_5COOCH_2CH_2CH_3 \arrow[r, shift left] \arrow[r, shift right, leftarrow] & C_6H_5CHO \arrow[d, shift right, leftarrow] \arrow[d, shift left] & + & CH_3CH_2CHO \arrow[r, shift left] \arrow[r, shift right, leftarrow] \arrow[d, shift right, leftarrow] \arrow[d, shift left] & CH_3CH_2COOCH_2C_6H_5 \quad (2) \\ & C_6H_5COOCH_2C_6H_5 & & CH_3CH_2COOCH_2CH_2CH_3 & \end{tikzcd}$$

Such a reaction explains the presence of benzyl benzoate among the reaction products from each ester. The absence of the esters derived from the aliphatic aldehyde might be expected on account of the susceptibility of such aldehydes to other types of condensation involving the hydrogens of the α-carbon atom.

A mixed aldol condensation between benzaldehyde and the aliphatic aldehyde appears to be a reasonable route to the formation of acetophenone and dibenzoylmethane (I) in the case of ethyl benzoate and to propiophenone together with ethylphenylcarbinol (II) in the case of *n*-propyl benzoate, *e. g.*

$$C_6H_5COOCH_2CH_3 \longrightarrow C_6H_5CHO + CH_3CHO \longrightarrow [C_6H_5CHOHCH_2CHO] \xrightarrow{-CO} C_6H_5CHOHCH_3 \xrightarrow{-2H} C_6H_5COCH_3 \xrightarrow[NaOC_2H_5]{C_6H_5COOC_2H_5} \underset{I}{(C_6H_5CO)_2CH_2} \quad (3)$$

$$C_6H_5COOCH_2CH_2CH_3 \longrightarrow C_6H_5CHO + CH_3CH_2CHO \longrightarrow [C_6H_5CHOHCH(CH_3)CHO] \xrightarrow{-CO} \underset{II}{C_6H_5CHOHCH_2CH_3} \xrightarrow{-2H} \underset{III}{C_6H_5COCH_2CH_3} \quad (4)$$

The loss of carbon monoxide from the proposed intermediates accounts for the evolution of this gas from the reaction mixture and associates its formation with that of the alkyl phenyl ketones and carbinols.[8]

(8) No precedent for the decomposition of the β-hydroxyaldehyde into carbon monoxide and the alkylphenylcarbinol could be found in the literature. 2-Methyl-3-hydroxyl-3-phenylpropanal resulting from a mixed aldol reaction between benzaldehyde and propionaldehyde has been reported [Haekhofer, *Monatsh.*, **22**, 96 (1901)] but was found to revert to the component aldehydes on heating. However, the conditions existing in the reaction mixture of the alkyl benzoate and sodium alkoxide could conceivably stabilize by esterification the hydroxyaldehyde against the reverse aldol reaction. The dehydrogenation of carbinols by alkoxides to ketones is, of course, a well-known reaction. It may seem that the formation of ketones, such as acetophenone, could be accounted for satisfactorily through the intermediate benzoylacetaldehyde, $C_6H_5COCH_2CHO$, formed through a Claisen condensation between ethyl benzoate and acetal-

TABLE I

MOLAR YIELDS OF PRODUCTS FROM THE REACTION OF FOUR MOLES OF $C_6H_5COOCH_2R$ WITH ONE MOLE OF RCH_2ONa AT 175–180°

RCH_2— is	Ester used, moles[a]	Benzoic acid, moles	RCH_2-OH, moles	1,3-Diketones, moles	Esters from Tischtschenko reaction, moles	$RCHOHC_6H_5$ and esters, moles	CO, moles	Products from Guerbet reaction, moles	Miscellaneous products, moles	Residue % of wt. of reacting ester
CH_3—	0.81	0.70	0.18	...	A[c] (0.01)	.....	..	.....	$(CH_3)_2O$ (0.55)	..
CH_3CH_2—	2.10	.55	1.80	I[b] (0.40)	A (.15)	.....	0.58	.....	$C_6H_5COCH_3$ (Trace)	4
$CH_3(CH_2)_2$—	2.60	.90	1.57	...	A (Trace)	II[b] (0.20) Benzoate of II (0.31)	1.07	IV[b] (0.04) Benzoate of IV (0.24)	$C_6H_5COC_2H_5$ (0.06) $C_6H_5CH{=}CHCH_3$ (Trace)	8
$(CH_3)_2CH$—	1.75	.60	1.80	I (.16) V (.08)	A (0.11)	.....	..	.....	$(CH_3)_2CO$ (Trace)	12
$CH_3(CH_2)_3$—	3.08	.85	1.27	...	A (.04)	VI (0.34) Benzoate of VI (0.41)	1.03	VII (0.10) Benzoate of VII (0.25)	$C_6H_5COC_3H_7(n)$ (0.07) $C_6H_5CH{=}CHC_2H_5$ (Trace)	3.6
$(CH_3)_2CHCH_2$—	3.00	1.02	1.42	...	A (.14) B[c] (.31)	VIII (0.19) Benzoate of VIII (0.27) Isobutyrate of VIII (0.02)	0.19	.....	$C_6H_5COC_3H_7(i)$ (0.28) $C_6H_5CH{=}C(CH_3)_2$[d] (0.03) $i\text{-}C_3H_7CHO$ (Trace) $i\text{-}C_3H_7COOH$ (Trace)	8.5
$(CH)_3CCH_2$	2.10	0.86	0.83	...	A (.14) C[c] (.12) D[c] (.80)	.....	..	.....	$(CH_3)_3CCHO$ (0.12) $(CH_3)_3CCOOH$ (0.14)	12.3

[a] These values were obtained by subtracting the moles of unchanged ester recovered from each reaction from the 4 moles of ester originally put into the reaction. [b] Roman numerals refer to compounds so designated in the text. [c] A is benzyl benzoate. B is isobutyl isobutyrate. C is benzyl trimethylacetate. D is neopentyl trimethylacetate. [d] A trace (0.7 g.) of a solid m. p. 143–146°, whose analyses (Table III) indicated that it was a dimer of $C_6H_5CH{=}C(CH_3)_2$, was isolated.

The presence of 2-methyl-1-pentanol (IV) among the reaction products of the *n*-propyl ester undoubtedly is due to a Guerbet reaction[9] between the *n*-propyl alcohol (or its ester) and the sodium propoxide

$$CH_3CH_2CH_2ONa + CH_3CH_2CH_2OH \longrightarrow NaOH + \underset{\text{IV}}{CH_3CH_2CH_2CH(CH_3)CH_2OH} \quad (5)$$

The absence of a 1,3-diketone among the reaction products of the propyl ester simply indicates that the propiophenone does not readily undergo a Claisen condensation.

The reasonableness of the above interpretation of the behavior of methyl, ethyl and *n*-propyl benzoates when heated with the corresponding alkoxides is confirmed by the results obtained with other alkyl benzoates. The nature and yields of the various reaction products obtained from the alkyl benzoates that were studied are summarized in Table I. The products from isopropyl benzoate are of particular interest. A reverse Tischtschenko reaction with this ester would produce benzaldehyde and acetone. The former compound appears as benzyl benzoate, while the acetone appears as such and as the 1,3-diketone, benzoylacetone (V), which is formed from a Claisen condensation of the ester and the ketone. The other diketone, dibenzoylmethane, is probably the result of an acyl exchange between isopropyl benzoate and benzoyl acetone:

$$C_6H_5COOCH(CH_3)_2 + CH_3COCH_3 \xrightarrow{NaOC_3H_7} \underset{\text{V}}{C_6H_5COCH_2COCH_3} + C_3H_7OH \quad (6)$$

$$C_6H_5COOCH(CH_3)_2 + C_6H_5COCH_2COCH_3 \longrightarrow (C_6H_5CO)_2CH_2 + CH_3COOCH(CH_3)_2$$

It is not improbable that the triacylmethane, acetyldibenzoylmethane, formed from benzoylacetone and isopropyl benzoate, may be an intermediate product in this acyl exchange. This type of acyl exchange is being investigated further. The absence of both carbon monoxide and the alkylphenylcarbinol type of condensation product adds more evidence to the proposed relationship between these two reaction products. It is seen from Table I that the undistillable residue from the reaction of this ester was quite high. Attempts to isolate benzal- and dibenzalacetone from this residue were unsuccessful.

The products obtained from the reaction of *n*-butyl benzoate with sodium *n*-butoxide parallel those obtained from the propyl ester. The yields of *n*-propylphenylcarbinol (VI) and 2-ethyl-1-hexanol (VII) together with their esters are quite high. It should be noted that, along with the high yield of (VI) and its ester, a cor-

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dehyde. However, neither this compound, prepared from ethyl formate and acetophenone, nor its sodium enolate loses carbon monoxide when heated to the temperatures used in these reactions.

[9] (a) Guerbet, *Compt. rend.*, **133**, 1220 (1902); (b) **134**, 467 (1903).

respondingly high yield of carbon monoxide is obtained.

$C_6H_5CHOHCH_2CH_2CH_3$ VI
$CH_3CH_2CH_2CH_2CH(C_2H_5)CH_2OH$ VII
$C_6H_5CHOHCH(CH_3)_2$ VIII

With isobutyl benzoate the aliphatic aldehyde, isobutyraldehyde, produced by the reverse Tischtschenko reaction, contains only one α-hydrogen atom. The data for this ester in Table I show that this aldehyde is actually formed and functions in a forward Tischtschenko reaction since a trace of isobutyraldehyde together with a substantial amount of isobutyl isobutyrate are found among the reaction products. The presence of isopropylphenylcarbinol (VIII) and carbon monoxide would be expected from the mixed aldol hypothesis developed above, but would seem to offer further evidence (*cf.* footnote 8) against the type of intermediate product that would result from a Claisen condensation of the ester with the aldehyde. The absence of the 8-carbon alcohol corresponding to the ones (IV and VII) obtained with *n*-propyl and *n*-butyl benzoate indicates that the β-hydrogen of isobutyl alcohol is not sufficiently active, under the conditions used in this work, to function in the Guerbet reaction (5). The small amounts of the hydrocarbons, isobutenylbenzene and its dimer, which were found are, no doubt, the result of the loss of benzoic acid from isopropylphenylcarbinyl benzoate during distillation.

A reverse Tischtschenko reaction with neopentyl benzoate would yield benzaldehyde and trimethylacetaldehyde. Since the latter aldehyde has no α-hydrogen, the only reaction products which could be expected on the basis of the above interpretation of the reaction are the esters resulting from forward Tischtschenko reactions involving the intermediate aldehydes. It is seen from the data in Table I that these esters, along with trimethylacetaldehyde and trimethylacetic acid, were obtained. The absence of both carbon monoxide and the alkylphenylcarbinol type of condensation product continues to point to a common precursor for these compounds.

From the foregoing data and discussion it appears that the reaction between the various alkyl benzoates and the corresponding sodium alkoxide at elevated temperatures can be explained satisfactorily through an initial reverse Tischtschenko reaction. Further condensation of the resulting aldehydes through forward Tischtschenko reactions (2) may produce new esters. A mixed aldol type of reaction between the two aldehydes, followed by the loss of carbon monoxide from the intermediate condensation product (reactions 3 and 4), accounts for alkylphenylcarbinols and ketones. It does not seem that Adickes' suggestion[5] that the alkyl phenyl ketone may result from a loss of formaldehyde from the ester is valid, since isopropyl benzoate which cannot undergo this type of decomposition gives 1,3-diketones and neopentyl benzoate which is structurally capable of losing formaldehyde does not appear to do so. Also, no indication of reaction products derived from formaldehyde was ever found in any of the reaction mixtures, and it may be seen in Table II that the quantities of reactants used in each reaction were, in most cases, quite satisfactorily recovered as reaction products. 1,3-Diketones. which are produced only with the ethyl and isopropyl benzoates, are the result of the condensation of the ester with ketones formed in the reaction mixture (reactions 3 and 6). With two of the esters, *n*-propyl and *n*-butyl benzoate, the Guerbet reaction (5) is prominent. Methyl benzoate stands apart from the other alkyl benzoates by reacting, in the main, with the alkoxide to give an ether (1). However, the presence of benzyl benzoate among the reaction products of this ester indicates that some of the Tischtschenko reaction had occurred.

The only other compound found in all of the reaction mixtures and whose formation remains to be explained is benzoic acid. This substance must be formed, in most part, by hydrolysis of the starting ester. The alcohol (RCH_2OH, Table I) which is obtained from each ester distils from the reaction mixture as the reaction proceeds. This fact, together with the relatively large quantities of sodium benzoate that are formed, strongly indicates saponification. The water (or sodium hydroxide) necessary for this saponification can be obtained from such reactions as the ether formation (1), the Guerbet reaction (5), and also from reactions, such as the crotonization of the aliphatic aldehydes, that produced the unidentified residues of each reaction.

Table II is a summary of the yields of those reaction products which are derived from the alkyl and from the benzoate portion of the two reactants. The yields of the products derived from the alkyl portion are expressed as per cent. of the sum of the reacting moles of ester and alkoxide, while those representing the benzoate portion are based on the moles of the benzoate ester entering into the reaction.

TABLE II

TOTAL YIELD OF PRODUCTS FROM THE REACTION OF ALKYL BENZOATES WITH SODIUM ALKOXIDES

Alkyl group is	Yield (%) of reaction products derived from the Alkyl portion	Benzoate portion
Methyl	71	89
Ethyl	71	80
n-Propyl	75	77
i-Propyl	74	70
n-Butyl	68	78
i-Butyl	71	78
Neopentyl	90	61

It is seen from the above table that most of the material put into the reaction was recovered as reaction products. Manipulation losses, intermediate fractions, and residues (see Table I) account for the differences between the above values and 100%. Only in the cases of methyl and neopentyl benzoates are the yields from the two portions of the reactants quite different. With the methyl ester the alkyl portion is low, indicating that it (or formaldehyde) is the more unstable. In the case of the neopentyl ester just the reverse is true. This ester gives the lowest yield of products derived from the benzoate portion of the ester, a fact which indicates that trimethylacetaldehyde is less susceptible than benzaldehyde to those condensations that take it into the reaction residues. Further evidence for such a conclusion was obtained from the reaction residues of this ester. From 18 g. of such residues, fractional distillation gave 7.2 g. of a solid substance which, after recrystallization from alcohol, melted at 103–104°. Analyses and molecular weight determinations showed the formula of this material to be $C_{18}H_{22}O$. Such a formula suggests an aromatic rather than an aliphatic ratio of carbon and hydrogen.

It should be pointed out that the reaction of certain types of ethyl esters with sodium ethoxide constitutes a quite satisfactory method for the preparation of the corresponding diacylmethane. Work in this Laboratory, which will be the subject of a future communication, has shown that difuroylmethane and dinicotinylmethane as well as dibenzoylmethane can be obtained in approximately 40% yields from the reaction of ethyl furoate and ethyl nicotinate with sodium ethoxide under proper conditions. The behavior of ethyl benzoate in this reaction also has suggested means of overcoming the difficulties associated with Claisen condensations involving acetophenone. If, for example, the condensation of ethyl benzoate with acetophenone by means of sodium ethoxide is carried out in the ordinary manner, very unsatisfactory yields of dibenzoylmethane result. These low yields are due, no doubt, to the loss of acetophenone through more rapid, alkali-catalyzed, competing reactions. However, if the alkoxide is added slowly to a mixture of ethyl benzoate and acetophenone which has been heated to 150°, the Claisen condensation is sufficiently rapid at this temperature to produce yields of the diketone as high as 70% of the theoretical.

Experimental

Materials Used.—Methyl. ethyl and *n*-propyl benzoates were prepared by esterifying benzoic acid with the alcohols in the presence of sulfuric acid. Isopropyl, *n*-butyl, isobutyl and neopentyl benzoates were prepared by heating the alcohols with benzoyl chloride until the evolution of hydrogen chloride ceased. The neopentyl alcohol was obtained by the reduction of ethyl trimethylacetate over copper–chromium oxide catalyst at 250° and under a pressure of 3000 atmospheres of hydrogen.[10] The other alcohols were purified commercial products. The alkyl benzoates that were used boiled within a two degree range and. with one exception. corresponded in properties to descriptions found in the literature. This exception was neopentyl benzoate. Beilstein, Vol. IX, 4th ed., p. 113, records the boiling point of this ester as 139–141°. No later reference to it could be found. The ester prepared in the present work distilled at 235–237° (740 mm.) or 110–111° (10 mm.): n^{25}_{D} 1.4875: d^{25}_{25} 0.9817.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.95: H. 8.39. Found: C, 75.05: H. 8.26.

The alkoxides were prepared by allowing 23 g. (1 atom) of finely powdered sodium, under ether, to react with a 5% excess of 1 mole of the alcohol. The ether suspension was stirred and refluxed until the reaction was complete. The ether was removed by distillation. and the remaining alkoxide heated under diminished pressure (10–15 mm.) in an oil-bath at 110–120° for two hours. after which time the ester was added to it and the following reaction carried out.

General Procedure for the Reaction of the Alkyl Benzoates with Sodium Alkoxides.—The 1-liter 3-necked flask containing the ester and alkoxide was fitted with a condenser for distillation and an efficient sealed stirrer. The stirrer was of a type that effectively mixed the reaction mixture even after it had become quite viscous. The flask was heated in an oil-bath kept at 175–180°. The evolution of alcohol and carbon monoxide from the reaction mixture became quite vigorous. The gas. after

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(10) Adkins and Folkers. THIS JOURNAL. 53, 1096 (1931).

passing through the condenser that condensed the alcohol. was led through twenty feet (6 meters) of copper coil cooled in an ice–salt or acetone–carbon dioxide snow mixture. Only in the case of dimethyl ether from the reaction of methyl benzoate was there any appreciable condensate from the copper coil. The gas finally was collected in a graduated bottle by displacement of an aqueous solution of sodium chloride.

When no more gas or distillate was evolved from the reaction (two to three hours). the oil-bath was removed and. with stirring maintained. the contents of the flask cooled to room temperature by running water. Then 250 cc. of water was added and the mixture transferred to a separatory funnel. A cooled solution of a 5% excess of sulfuric acid in 250 cc. of water was added and after vigorous shaking the ester layer was separated and washed with 200 cc. of water. This ester layer was then shaken with 300 cc. of a saturated sodium bicarbonate solution until the evolution of carbon dioxide ceased. The ester layer was again separated and washed with 200 cc. of water. The bicarbonate solution was extracted with 150 cc. of ether and the ether extract combined with the ester layer. The ether–ester mixture was dried over anhydrous sodium sulfate. The acids formed in the reaction were obtained from the bicarbonate solution by acidification with dilute sulfuric acid.

The distillate from the reaction and the ethereal solution of the reaction products. after removal of the ether, were fractionated separately. The fractionation was carried out with a 15-cm. Widmer column. Each fraction was distilled through the column at least twice and in certain cases four or five times.

The carbon monoxide in the gas that was collected was determined in the usual way. by absorption in cuprous chloride solution. When any considerable quantity of gas was evolved from a reaction it was generally found to be 95–99% carbon monoxide. The remainder of the evolved gas appeared to be unsaturated hydrocarbons.

Separation and Identification of Reaction Products.— In the case of the methyl ester the methyl alcohol was condensed by the water condenser while the dimethyl ether was condensed by the copper coil surrounded by an acetone–carbon dioxide snow mixture. The ether was identified by its boiling point. −22°.[5]

Acetophenone from the reaction of the ethyl ester was converted into the phenylhydrazone. m. p. 102–103°. Benzyl benzoate was obtained as a fraction boiling at 160–165° (6 mm.) which contained a small amount of dibenzoylmethane. The latter compound was removed by washing with 20% sodium hydroxide solution. The ester thus purified boiled at 154–158° (4 mm.). gave a 92% yield of benzoic acid and benzyl alcohol. b. p. 200–205°. 3.5-dinitrobenzoate, m. p. 112–113°,[11] α-naphthylurethan. m. p. 132–133°.[12] Dibenzoylmethane was obtained as a solid fraction boiling just above the benzyl benzoate. It was identified by its m. p.. 78–79°: dibromide, m. p. 94°; 2,3,5-triphenylpyrazole, m. p. 137°; and by hydrolysis to benzoic acid and acetophenone.[13]

The distillate from the isopropyl ester yielded about 0.5 cc. of acetone, b. p. 55–57°: dibenzal derivative, m. p. 113°. The benzoylacetone was obtained as a solid fraction boiling at 135–140° (15 mm.). It gave a grayish-black copper salt. m. p. 190–191°.[14] The benzyl benzoate and dibenzoylmethane were identified as described above. Only 400 cc. of gas. which contained no carbon monoxide. was obtained from the reaction of the isopropyl ester.

The 2-methyl-1-pentanol was present both in the distillate and among the products remaining in the reaction flask of the *n*-propyl ester. This alcohol boiled at 145–146° and yielded an α-naphthylurethan (Table III). It was converted by oxidation with permanganate[9a] into 2-methylpentanoic acid. which also was prepared from methylmalonic ester and *n*-propyl bromide.[15] The *p*-phenylphenacyl esters (Table III) of the two specimens of acids were identical. The benzoate of 2-methyl-1-pentanol was obtained from the reaction products as a fraction boiling at 100–105° (2 mm.). It was purified further by several fractionations (Table III). Propiophenone, ethylphenylcarbinol and unchanged ester were found in a fraction boiling below the *n*-propyl benzoate. The ester was removed by saponification and the relative amounts of ketone and carbinol in the unsaponifiable material determined from the refractive index of the mixture. The values so obtained were checked by the value found for the alcohol with the Grignard machine. The propiophenone was identified as the semicarbazone. m. p. 177–178°.[16] and the ethylphenylcarbinol as the α-naphthylurethan. m. p. 100–101°.[12] The benzoate of ethylphenylcarbinol was obtained as a fraction boiling at 150–160° (4 mm.). It was purified by further fractionation and compared with the benzoate of the carbinol synthesized from benzaldehyde and ethylmagnesium bromide (Table III). The benzoate of ethylphenylcarbinol decomposes slightly on distillation into benzoic acid and propenylbenzene which boils at 170–175°. This unsaturated hydrocarbon was identified as its dibromide. m. p. 67–68°.[17]

The liquid products from the reaction of the *n*-butyl ester were fractionated five times. 2-Ethyl-1-hexanol which distilled at 179–182°[9b] was converted into the α-naphthylurethan (Table III) and 2-ethylhexanoic acid by oxidation with permanganate. From this acid the amide. m. p. 103°,[18] and the *p*-phenylphenacyl ester (Table III) were prepared. This acid also was prepared from *n*-butylmalonic ester and ethyl bromide. The synthetic product gave an amide and *p*-phenylphenacyl ester identical with those obtained from the oxidation product of 2-ethyl-1-hexanol from the reaction. The benzoate of 2-ethyl-1-hexanol was collected in the fraction that boiled at 125–131° (3 mm.). This material after refractionation had the properties listed in Table III. Butyrophenone and *n*-propylphenylcarbinol were found in a fraction containing some unchanged *n*-butyl benzoate. The ester was removed from this fraction by saponification and the ketone and carbinol determined as were the corresponding compounds from the *n*-propyl ester. The semicarbazone of the ketone melted at 187–188°.[19] The carbinol was iden-

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[11] Kamm. "Qualitative Organic Analysis." 2d ed., John Wiley and Sons. Inc., New York, N. Y., p. 166.

[12] Bickel and French. THIS JOURNAL. **48**. 749 (1926).

[13] *Cf.* Wislicenus. *Ann.*, **308**. 246–253 (1899).

[14] Wislicenus and Stober. *Ber.*, **35**. 545 (1902).

[15] Lieben. *Monatsh.*, **4**. 25 (1883).

[16] Shriner and Turner. THIS JOURNAL. **52**. 1269 (1930).

[17] Rügheimer. *Ann.*, **172**. 131 (1874).

[18] Raper. *J. Chem. Soc.*, **91**. 1837 (1907).

[19] Sorge. *Ber.*, **35**. 1074 (1902).

TABLE III

PROPERTIES AND ANALYSES OF MISCELLANEOUS NEW COMPOUNDS

Compound	Formula	M. p., °C.	B. p., °C. (mm.)	d^{25}_{25}	n^{25}_D	Analyses, % Calcd. C	H	N	Found C	H	N
α-Naphthylurethan of 2-methyl-1-pentanol	$C_{17}H_{21}O_2N$	75–76	.....	....	....			5.2			5.1
Benzoate of 2-methyl-1-pentanol	$C_{13}H_{18}O_2$	.....	130–132 (9)	0.9828	1.4919	75.64	8.85		75.40	8.50	
Benzoate of ethylphenylcarbinol[a]	$C_{16}H_{16}O_2$	.....	146–147 (3)	1.0806	1.5499	79.96	6.72		80.21	6.72	
Benzoate of ethylphenylcarbinol[b]	$C_{16}H_{16}O_2$	.....	134–135 (1)	1.0814	1.5491				80.12	6.90	
α-Naphthylurethan of 2-ethyl-1-hexanol	$C_{19}H_{25}O_2N$	60–61	.....	....	....			4.7			4.6
Benzoate of 2-ethyl-1-hexanol	$C_{15}H_{22}O_2$	.....	119–120 (2)	0.9694	1.4918	76.86	9.47		76.83	9.33	
p-Phenylphenacyl ester of 2-methylpentanoic acid	$C_{20}H_{22}O_3$	64–65	.....	....	....	77.38	7.15		77.12	7.44	
p-Phenylphenacyl ester of 2-ethylhexanoic acid	$C_{22}H_{26}O_3$	53–54	.....	....	....	78.06	7.75		77.95	7.91	
α-Naphthylurethan of propylphenylcarbinol	$C_{21}H_{21}O_2N$	98–99	.....	....	....			4.4			4.5
Benzoate of propylphenylcarbinol[c]	$C_{17}H_{18}O_2$	.....	144–145 (2)	1.0590	1.5442	80.27	7.14		80.48	7.19	
Benzoate of propylphenylcarbinol[d]	$C_{17}H_{18}O_2$	.....	145–146 (2)	1.0683	1.5446				80.44	7.12	
α-Naphthylurethan of *i*-propylphenylcarbinol	$C_{21}H_{21}O_2N$	116–117	.....	....	....			4.4			4.4
Benzoate of *i*-propylphenylcarbinol[e]	$C_{17}H_{18}O_2$	.....	148–149 (3)	1.0644	1.5460	80.27	7.14		80.28	7.22	
Benzoate of *i*-propylphenylcarbinol[f]	$C_{17}H_{18}O_2$	.....	137–138 (2)	1.0696	1.5450				80.17	7.00	
Dimer of isobutenylbenzene[g]	$C_{20}H_{24}$	150–151	.....	....	....	90.91	9.09		90.33	9.88	
Solid from neopentyl run[h]	$C_{18}H_{22}O$	103–104	.....	....	....	85.04	8.66		85.03	8.60	

[a] From reaction. [b] From benzaldehyde and ethylmagnesium bromide. [c] From reaction. [d] From benzaldehyde and *n*-propylmagnesium bromide. [e] From reaction. [f] From isopropylmagnesium bromide and benzaldehyde. [g] Molecular weight (Rast), 265. [h] Molecular weight (Rast), 247.

fied by oxidation to butyrophenone and also as the α-naphthylurethan (Table III). This derivative was identical with the α-naphthylurethan of the carbinol obtained from the reaction of benzaldehyde with *n*-propyl bromide. The benzoate of *n*-propylphenylcarbinol appeared in a fraction boiling at 158–164° (4 mm.). Its properties compared quite satisfactorily (see Table III) to those of the benzoate of the synthetic carbinol. This benzoate decomposed slightly during distillation to benzoic acid and butenylbenzene.[20] A small amount (4.2 g.) of this latter product, which boiled at 180–185°, was found among the reaction products of the *n*-butyl ester. It was identified as the dibromide, m. p. 72–73°.[21]

From the reaction of isobutyl benzoate with the sodium isobutoxide, both isobutyraldehyde (0.5 g.) and isobutyl isobutyrate were found with isobutyl alcohol in the distillate from the reaction. The aldehyde was identified as the 2,4-dinitrophenylhydrazone, m. p. 180–181°.[22] The isobutyl isobutyrate boiled at 144–148°. It was identified by hydrolysis to the acid and alcohol. Isobutyric acid (4.2 g.) was found along with the benzoic acid from the reaction. It was identified as the *p*-toluidide, m. p. 102–103°.[23] Isobutyrophenone and isopropylphenylcarbinol were found along with isobutyl benzoate as one of the fractions. These products were estimated as were the corresponding ketone and carbinol in a similar mixture from the *n*-propyl and *n*-butyl ester. The semicarbazone and the oxime of the isobutyrophenone melted at 180–181°[24] and 61–62°, respectively.[25] Isopropylphenylcarbinol was synthesized from benzaldehyde and isopropylmagnesium bromide and its α-naphthylurethan compared with the same derivative of the carbinol obtained from the ester reaction (Table III); they were identical. The benzyl benzoate from this run was in a fraction boiling at 142–148° (3 mm.) which also contained some of the benzoate of isopropylphenylcarbinol. The amounts of these two esters in the fraction were determined by saponification and separation by fractionation of the resulting benzyl alcohol and isopropylphenylcarbinol. The main portion of the benzoate of isopropylphenylcarbinol was obtained, after several fractionations, as a fraction boiling at 148–149° (3 mm.). It corresponded in properties to the benzoate prepared from the synthesized carbinol (see Table III). A small amount of an ester mixed with isobutyl benzoate was obtained as a fraction boiling higher [103–108° (4 mm.)] than isobutyl benzoate. This fraction on saponification yielded isobutyric acid, isopropylphenylcarbinol, isobutyl alcohol and benzoic acid, showing that it was a mixture of isopropylphenylcarbinyl isobutyrate with the starting ester. As in the other cases, the benzoate of isopropylphenylcarbinol decomposed somewhat on distillation to yield benzoic acid and isobutenylbenzene. Such a decomposition accounts for the presence of this hydrocarbon among the reaction products. It boiled at 173–177°, yielded a liquid dibromide but a solid nitrosite with sodium nitrite and acetic acid.[26] From the residues of the isobutyl run a solid which analyses indicated to be a dimer of isobutenylbenzene was obtained (Table III).

Trimethylacetaldehyde was found in the distillate of the neopentyl run. It was in a fraction boiling at 70–80°. The semicarbazone and 2,4-dinitrophenylhydrazone melted at 189–190°[27] and 208–209°[23], respectively. Trimethylacetic acid was separated from the benzoic acid by steam distillation. It boiled at 158–160°; amide, m. p. 153–154°.[28] The neopentyl trimethylacetate fraction boiled

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[20] *Cf.* Klages, *Ber.*, **31**, 1003 (1898).

[21] Perkin, *J. Chem. Soc.*, **32**, 667 (1877).

[22] Allen, THIS JOURNAL, **52**, 2957 (1930).

[23] Bischoff, *Ann.*, **279**, 173 (1894).

[24] Lapworth and Steele, *J. Chem. Soc.*, **99**, 1885 (1911).

[25] Rattner, *Ber.*, **20**, 506 (1887).

[26] Angeli, *ibid.*, **25**, 1962 (1892).

[27] Beilstein, Supplement I, 4th ed., 1928, p. 354.

[28] Franchimont and Klobbie, *Rec. trav. chim.*, **6**, 238 (1887).

at 162–164°.[29] The benzyl benzoate fraction boiled at 145–151° (4 mm.). Benzyl trimethylacetate was obtained mixed with neopentyl benzoate as a fraction boiling at 113–118° (15 mm.). The amounts of each of the esters in this fraction were determined by saponification and determination of the quantities of the respective alcohols and acids. From the residues of the reaction of this ester a solid, which crystallized from alcohol in fine white needles, was obtained. Analytical data (Table III) indicated that this substance had the molecular formula $C_{11}H_{22}O$. No further work was done with this material.

Summary

A study of the reaction of various alkyl benzoates with the corresponding sodium alkoxides is reported. The simplest reaction occurs with the methyl ester and produces dimethyl ether and sodium benzoate. The reaction products from the other alkyl benzoates that were studied are explained by two general reaction courses: (1) a reverse Tischtschenko reaction that yields benzaldehyde and an aliphatic aldehyde (or ketone if the alkyl group is secondary); the resulting aldehydes then enter into further condensations such as forward Tischtschenko reactions to yield new esters or mixed aldol condensations to yield alkylphenylcarbinols and ketones. In the cases of the ethyl and isopropyl esters the ketones produced in the reaction yield 1,3-diketones by further condensation with the starting ester; (2) the condensation of an alcohol (or its ester) with the sodium alkoxide through the Guerbet reaction.

The relatively large quantities of sodium benzoate that are formed in each reaction are attributed to saponification of the starting esters by water produced in the various reactions which occur.

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[29] Samec, *Ann.*, **351**, 261 (1907).

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Thermodynamic Properties of the Hexyl Alcohols. II. Hexanols-1, -2, -3 and 2-Methylpentanol-1 and -4

BY FRANK HOVORKA, HERMAN P. LANKELMA AND SPENCER C. STANFORD[1]

This paper represents the second[2] of a series of investigations being carried out in this Laboratory on the relations between the physical properties and the chemical constitution of the hexyl alcohols, and concerns the viscosity, vapor pressure, surface tension, density and refractive index of hexanols-1, -2, -3, and 2-methylpentanols-1 and -4.

Preparation of Materials.—Satisfactory methods of preparation are described in the literature for each of the alcohols concerned. Each alcohol, with the exception of 2-methylpentanol-4, was made by the Grignard synthesis, as follows: hexanol-1 from *n*-butyl bromide and ethylene oxide,[3] hexanol-2 from *n*-butyl bromide and acetaldehyde,[4] and hexanol-3 from *n*-propyl bromide and propionaldehyde. Pickard and Kenyon[5] prepared hexanol-3 from *n*-propyl chloride and propionaldehyde. 2-Methylpentanol-1 was prepared from formaldehyde and 2-chloropentane.[6] 2-Methylpentanol-4 was prepared by the reduction of methyl isobutyl ketone with sodium in ethyl alcohol according to the directions given by Neely.[7]

Purification.—The preliminary fractional distillations were carried out using a column 40 cm. long filled with glass beads. This column was equipped with a liquid divider still head and was heated externally by means of a nichrome wire heater.

The final fractional distillations were performed in a similar column, 70 cm. long equipped throughout with Pyrex ground glass joints.

Aluminum amalgam was used as the drying agent.[8] It proved satisfactory for all the alcohols except hexanol-2. When used with this alcohol there apparently was some decomposition to the corresponding olefin, as evidenced by a decided decrease in the boiling point with time. The final fractional distillation of this substance was, therefore, carried out in the absence of the drying agent.

The temperature ranges were read on a Beckmann thermometer which was suspended inside the column. The alcohols were considered to be sufficiently pure when the boiling point range did not exceed 0.04°.

Apparatus. Temperature Control.—The temperature was controlled to ±0.01° up to about 55°. At the highest temperatures used (150–160°) the maximum variation was not over ±0.05°, and such variations were not of long duration, hence the control was of the order of ±0.02° up to the highest temperature measured.

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[1] This article represents a part of a dissertation submitted by Spencer C. Stanford to the Graduate School, Western Reserve University, May, 1935, in partial fulfilment of the degree of Doctor of Philosophy.

[2] Hovorka, Lankelma and Naujoks, THIS JOURNAL, **55**, 4820 (1933).

[3] Dreger, *Org. Syntheses*, **6**, 54 (1926).

[4] Norris and Cortese, THIS JOURNAL, **49**, 2640 (1927).

[5] Pickard and Kenyon, *J. Chem. Soc.*, **103**, 1923 (1913).

[6] Przewalski, *J. Russ. Phys.-Chem. Soc.*, **40**, 1105 (1908).

[7] Neely, unpublished Master's Thesis, Western Reserve University, 1931.

[8] Brunel, Crenshaw and Tobin, THIS JOURNAL, **43**, 561 (1921).