firmed by comparison of the physical properties of carefully purified material.

2. The formulation of narceine as $C_{23}H_{27}NO_8 \cdot 3H_2O$ has been definitely established by quantitative determination of the water of crystallization content and analyses of the dehydrated material.

3. Dihydronarceonic acid, its methyl ester and the methyl and ethyl esters of narceonic acid have been prepared.

4. Although attempts to alkylate the methylene group and to effect the reduction of the CO group by catalytic hydrogenation were unsuccessful, the lack of active hydrogen in methyl dihydronarceonate, its behavior on bromination and the formation of narceine methoxime confirm the formulation of narceine as a highly substituted desoxybenzoin.

RAHWAY, NEW JERSEY

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, MONSANTO CHEMICAL WORKS]

The Reaction between Acid Chlorides and Ethers in the Presence of Zinc Chloride

BY L. P. KYRIDES

Descudé[1] reported that on mixing acetyl chloride and anhydrous ethyl ether with a sufficiently large amount of zinc chloride a violent reaction took place immediately which needed to be kept under control by means of external cooling. On working up the reaction mixture he obtained ethyl acetate and ethyl chloride in yields approximating 90 and 67%, respectively, on acetyl chloride, based on the equation

$$CH_3COCl + (C_2H_5)_2O \longrightarrow CH_3CO_2C_2H_5 + C_2H_5Cl$$

The author, furthermore, makes the statement that "the yields are almost theoretical."

Wedekind and Hauessermann[2] obtained a 50% yield of ethyl benzoate from benzoyl chloride and excess of ether in presence of large amounts of sublimed ferric chloride.

Recently H. W. Underwood, Jr., has extended the study of this reaction, stressing the catalytic action of zinc chloride. He and Wakeman[3] have refluxed the acid chlorides mixed with a slight excess of anhydrous ethers in presence of relatively substantial amounts of zinc chloride and isolated the corresponding esters in some instances in as high as 79% of the theoretical yield.

The amount of alkyl chlorides isolated by Underwood and Toone[4] was far from that which is required by Descudé's equation. The authors, in

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(1) Descudé, *Compt. rend.*, **132**, 1129 (1901).

(2) Wedekind and Haussermann, *Ber.*, **34**, 2081 (1901).

(3) Underwood and Wakeman, THIS JOURNAL, **52**, 387 (1930).

(4) Underwood and Toone, *ibid.*, **52**, 391 (1930).

discussing the action of zinc chloride on ethers, indicate that the ether is decomposed into alcohol and an alkylene. If an acid chloride is present it reacts with the alcohol to form an ester, while the liberated hydrochloric acid reacts with some alcohol to produce the alkyl chloride. Accordingly, based on the mechanism of the reaction as outlined, the amount of the ester formed cannot possibly exceed that which is equivalent to the unsaturated hydrocarbon; while the alkyl chloride, being a by-product, can be formed only in relatively small amounts. The authors isolated the alkyl chlorides in yields not much over 30% of the theoretical.

Because of the discrepancy between Descudé's statement and the results obtained by Underwood and his co-workers, it seems desirable that a quantitative isolation of the products of the reaction should be made.

In our case, where we used a mere trace of zinc chloride, the reaction between benzoyl chloride and ethyl ether gave results substantially as indicated in the equation given above.

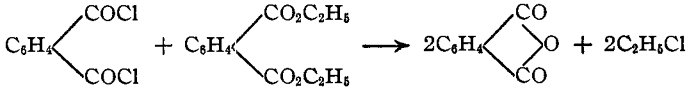
In the case of other ethers, the amounts of alkyl chlorides isolated will be less, since these chlorides have a greater tendency to decompose into an alkylene and hydrochloric acid.

In the case of *o*-phthalyl chloride, Underwood and Wakeman observed that it reacts with ethyl ether in the presence of zinc chloride to form large amounts of phthalic anhydride together with a small amount of diethyl phthalate, and they conclude that the results "indicate that diethyl phthalate may be transformed into phthalic anhydride by zinc chloride."[5]

In order to avoid any side reactions which might be induced by the catalyst, we have used only traces of it in the reactions studied.

We have observed that the chlorides of the monocarboxylic acids in reaction with ether in the presence of traces of zinc chloride require higher temperatures and longer time for completion than phthalyl chloride. With low boiling acid chlorides such as butyryl chloride, the reaction is hardly noticeable even at boiling temperature. Higher boiling acid chlorides, such as lauryl and benzoyl chlorides, show a distinct rate of reaction above 140°. By slowly dropping ether into benzoyl chloride containing traces of zinc chloride above 140°, we were able to isolate ethyl benzoate and ethyl chloride in good yields following the equation given above.

In the case of *o*-phthalyl chloride, the reaction product does not contain any appreciable amount of the expected diethyl phthalate, due to the fact that the latter reacts readily with phthalyl chloride in the presence of zinc chloride to give two moles of ethyl chloride as follows



$$C_6H_4\left\langle\begin{matrix}COCl\\COCl\end{matrix}\right. + C_6H_4\left\langle\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}\right. \longrightarrow 2C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + 2C_2H_5Cl$$

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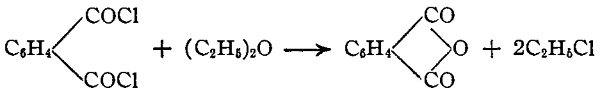
(5) See also Underwood and Baril, THIS JOURNAL, 52, 396 (1930).

so that the final result of the reaction may be expressed by the equation



$$C_6H_4(COCl)_2 + (C_2H_5)_2O \longrightarrow C_6H_4(CO)_2O + 2C_2H_5Cl$$

Experimental

(1) **Reaction between Benzoyl Chloride and Ethyl Ether.**—One hundred and fifty grams of benzoyl chloride (1.06 g. moles) and 0.5 g. of technical anhydrous zinc chloride were charged into a three-necked, 500-cc. flask carrying a very efficient spiral reflux condenser, dropping funnel and thermometer. The flask was heated and the reaction temperature maintained at about 150°; 90 g. (1.21 g. moles) of freshly distilled ethyl ether was dropped in over a period of about ten hours at such a rate that the temperature could be maintained at the point indicated. Toward the end of the addition of the ether, the reaction temperature was raised to 170°. The reaction gases were cooled through the reflux spiral condenser, which was kept at the boiling point of ethyl chloride by running cold water, and, after bubbling through water, were condensed by means of a spiral condenser kept at 0° and collected in a receiver cooled at about −5°.

The liquid which was collected was fractionated carefully from small amounts of ethyl ether through an efficient spiral condenser maintained at 12° by running cold water. In this manner 54 g. of ethyl chloride boiling at 12° (a few drops up to 16°) was collected. This is equivalent to 78.0% yield.

The residue from the distillation was fractionated directly *in vacuo:* 146.5 g. of colorless ethyl benzoate was obtained boiling at 96 to 98° at about 20 mm. This is equivalent to a 91.5% yield from benzoyl chloride. The product was free from any odor of benzoyl chloride and on analysis showed minute traces only of chlorine.

The ester, upon fractionation at atmospheric pressure, boiled to the extent of 97% at 208°.

In the above reaction a small amount of uncondensed combustible gas escaped, which was undoubtedly ethylene. Allowing for unavoidable losses in the handling of ethyl chloride, it appears evident that Descudé's equation is substantially correct.

Lauryl chloride reacts similarly but very slowly with ether at its boiling point.

(2) **Phthalyl Chloride and Ethyl Ether.**—Two hundred and fifty grams (1.18 g. moles) of phthalyl chloride (analyzing 96%) and 0.4 g. of zinc chloride were charged into a three-necked flask (connected as under benzoyl chloride). The mixture was heated at 110° in the beginning and the temperature gradually raised to 170° as the reaction progressed, in order to avoid crystallization of the phthalic anhydride; 110 g. (1.48 g. moles) of ethyl ether was dropped in over a period of three hours. The ethyl chloride formed was fractionated in the presence of water through a spiral condenser maintained at 12°; 137 g. of distillate was obtained boiling up to 20°. This was redistilled and 122 g. of liquid was collected boiling at 12° (a few drops up to 14°). The latter amount is equivalent to an 80% yield on phthalyl chloride assuming that two molecules of ethyl chloride are formed per mole of phthalyl chloride and ether.

(3) **Phthalyl Chloride and Isopropyl Ether.**—Two hundred grams (0.946 g. mole) of phthalyl chloride (96%) and 0.5 g. of zinc chloride were heated at 130 to 140° at first and then gradually raised to 170° during the reaction. The reflux spiral condenser in this case was cooled by a slow current of running water so that any isopropyl chloride formed would distil over. The reaction products were cooled with ice water; 110 g. (1.08 g. moles) of isopropyl ether (freshly distilled) was dropped in within six hours. In this case it was observed that a considerable amount of gas, which was undoubtedly propylene, escaped condensation. In order to eliminate the presence of any hydrochloric acid in the condensate, even after bubbling the gases through warm water be-

fore condensation, the condensate was shaken with cold water and distilled. The wet distillate was dried over calcium chloride and refractionated. The isopropyl chloride obtained in this manner weighed 92 g., which is equivalent to a yield of 62% from phthalyl chloride. The low yield of chloride is explained by the fact that isopropyl chloride readily undergoes decomposition to propylene and hydrochloric acid.

Summary

The chlorides of high boiling monocarboxylic acids react with ethyl ether in the presence of traces of zinc chloride. With benzoyl chloride, ethyl chloride and the ester are obtained in good yield.

Equimolecular amounts of *o*-phthalyl chloride and ethyl ether react to give phthalic anhydride and approximately two molecules of ethyl chloride.

o-Phthalyl chloride and isopropyl ether react similarly to give phthalic anhydride and isopropyl chloride, but in this case larger amounts of propylene are formed as a by-product.

ST. LOUIS, MISSOURI

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The Halogenation of Meta-Diphenylbenzene. I. The Monochloro and Monobromo Derivatives

BY WALTER A. COOK AND KATHRYN HARTKOFF COOK

In the commercial manufacture of biphenyl from benzene, considerable quantities of the meta and para isomeric diphenylbenzenes are formed as by-products, the meta isomer predominating. Very little is reported in the literature on derivatives of the latter hydrocarbon. Olgiati[1] described the monobromo and tetrabromo derivatives and others the trinitro and triamino derivatives.[2] Recently, Wardner and Lowy[3] reported the synthesis of the mononitro, the dinitro and related compounds. In no case, however, has sufficient experimental proof been advanced to establish completely the structures of the above-mentioned derivatives.

This paper is limited to an account of the monochloro and monobromo derivatives, their oxidation products, and their proof of structure. A later publication will describe the preparation and properties of the polychloro and polybromo derivatives. Further study of the applications of the monohalogen derivatives to the Grignard reaction and the synthesis of metallo organo compounds, including the mercury and arsenic types, has been planned, and work in that direction is being pursued in this Laboratory.

The authors acknowledge their great indebtedness to Mr. R. E. Bowman of Wilmington, Delaware, for the generous supply of purified *m*-diphenyl-

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(1) Olgiati, *Ber.*, **27**, 3385 (1894).

(2) Schultz and Schmidt, *Ann.*, **203**, 118 (1880).

(3) Wardner and Lowy, THIS JOURNAL, **54**, 2510 (1932).