

onic ester, and benzyl cyanide. It also combines readily with *p*-toluene-sulfinic acid.

2. With cyano-acetic ester no substance composed of one molecule of each of the components could be obtained, the sole product being a trimolecular substance containing one molecule of the ester to two of the ketone. Cyanopropionic ester and benzyl cyanide gave the normal addition products that were to be expected; but these proved to be ill adapted for studying the unsaturated system that is responsible for the peculiarities of the glutaconic acids.

3. *p*-Toluene sulfinic acid gives two isomeric unsaturated sulfones.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THE PREPARATION OF ALKYL CHLORIDES

BY JAMES F. NORRIS AND HAZEL B. TAYLOR

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The conversion of alcohols into alkyl halides by means of aqueous solutions of hydrochloric, hydrobromic and hydriodic acids has been described in papers previously published from this Laboratory.¹

All the alcohols studied were converted into bromides and iodides when they were heated in an open vessel with an aqueous solution of the corresponding hydrogen halide. The yields of the halides obtained were excellent when the constant-boiling solutions of the acids were used; and the products obtained were free from impurities. This method of preparing alkyl bromides and iodides has, consequently, come into general use.

Only a few of the large number of alcohols studied were converted into chlorides when they were boiled with aqueous hydrochloric acid. The method could not be applied to the saturated primary alcohols. Tertiary alcohols, some secondary alcohols, and certain primary compounds in which the hydroxyl group was activated by the presence of a neighboring negative radical did, however, furnish satisfactory yields of chlorides.

We have recently returned to the study of the reaction in the hope of discovering the conditions necessary to prepare alkyl chlorides from the primary saturated alcohols. As the result of the investigation of certain condensations through the aid of zinc chloride, it seemed probable that the latter reagent does not act, as has been supposed in the past, as a dehydrating agent when it is used in the preparation of alkyl chlorides from alcohols and hydrogen chloride. Zinc chloride markedly activates the carbon-oxygen bond in ethers, esters and anhydrides, and makes it possible to bring about reactions between these substances and other compounds.

¹ *Am. Chem. J.*, **38**, 627 (1907); *THIS JOURNAL*, **38**, 1071 (1916); **42**, 2093 (1920).

It seemed probable, therefore, that the role played by zinc chloride in the preparation of alkyl chlorides in non-aqueous solutions was, in part, that of a catalytic reagent, which functioned through the formation of a molecular compound of the alcohol and the metallic chloride. The condensation of this molecular compound with hydrogen chloride was rendered possible as the result of the activation of the hydroxyl group. If the above view were correct, the reaction of an alcohol with hydrogen chloride might take place in the presence of water, provided an adequate amount of the molecular compound could be maintained in the solution.

Experiments designed to test this hypothesis led to very satisfactory results. The first work was carried out with *iso*amyl alcohol because it was found that the distillation of the alcohol with concd. hydrochloric acid alone yielded no chloride. A series of experiments with various amounts of the acid and zinc chloride led to the conclusion that as the proportion of the metallic chloride was increased, the yield of amyl chloride increased. Since the molecular compound of the alcohol and zinc chloride is largely decomposed in the presence of aqueous hydrochloric acid, a relatively large amount of the metallic chloride is required to obtain a good yield of amyl chloride. It was found that satisfactory results were obtained with the alcohols studied when they were treated in the molecular ratio of one of alcohol, two of zinc chloride, and two of hydrogen chloride in the form of concd. hydrochloric acid.

It was shown that the formation of the alkyl chlorides in this way was not due to the fact that the presence of zinc chloride raised the boiling point of the mixture of reacting substances. The same temperature can be reached with calcium chloride, but under these conditions the alkyl chlorides are not formed. The behavior of a number of chlorides was studied. Only mercuric chloride and stannous chloride produced any effect, and in either case it was small.

In the case of all the alcohols, more or less of high-boiling products were formed. It was found that these were completely destroyed when the chlorides were refluxed with concd. sulfuric acid. The lower primary and secondary alkyl chlorides can be distilled directly from concd. sulfuric acid with only a very slight loss. This method of treatment readily yields a purer product than that obtained by a long fractional distillation.

The following alcohols have been converted into chlorides by treatment with concd. hydrochloric acid and zinc chloride: methyl, ethyl, *n*-propyl, *isopropyl*, *n*-butyl, *sec*-butyl, *iso*amyl, pentanol-2, cetyl, β -phenylethyl, γ -phenylpropyl, *m*-nitrobenzyl, and *p*-nitrobenzyl. The yields of the purified chlorides varied from 60 to 70%. *iso*Butyl alcohol was converted largely into products that boiled at a high temperature. In the case of this alcohol dehydration and polymerization probably took place. In this alcohol there is adjacent to the hydroxyl group a hydrogen linked to

a tertiary carbon atom. This arrangement is favorable to the formation of an unsaturated compound. The best yield of *isobutyl* chloride obtained was 15%.

The method of preparing alkyl chlorides described above is preferable to the older one in which a mixture of the alcohol and zinc chloride is treated with hydrogen chloride in the absence of water. It is evidently more convenient to work with concd. hydrochloric acid than with hydrogen chloride, but there are advantages other than this. In the older method dehydration of the alcohol takes place to some extent and a secondary halide is formed in the case of the higher primary alcohols as the result of the addition of the hydrogen chloride and the olefin produced. This reaction takes place to but a slight degree, if at all, when water is present.

The hypothesis given above as to the mechanism of the reaction, namely, that zinc chloride activates the carbon-oxygen bond in the presence of water led to the study of the behavior of ethers and esters when heated in an open vessel with hydrochloric acid and zinc chloride. It was found that *n*-butyl ether and *isoamyl* acetate yielded the corresponding alkyl halide when distilled with a mixture of zinc chloride and concd. hydrochloric acid. The chlorides are not obtained in the absence of zinc chloride. This reaction is being studied further.

Experimental Part

General Procedure.—A series of experiments with *isoamyl* alcohol led to the conclusion that the most satisfactory results were obtained when the reaction was carried out with a mixture of the alcohol, concd. hydrochloric acid and zinc chloride in the molecular ratio of 1 to 2 (HCl) to 2, respectively.

The method of procedure was the same in all cases except those noted below, and can be illustrated by a description of an experiment with *isoamyl* alcohol. One-quarter mole of the alcohol was used in each experiment. The weights in the case of *isoamyl* alcohol were alcohol 22 g., concd. hydrochloric acid 47 g., anhydrous zinc chloride 68 g. The zinc chloride was dissolved in the cooled acid to prevent loss of hydrogen chloride; the alcohol was then added and the mixture was refluxed for one hour. The mixture was then distilled as long as an insoluble oil passed over. The latter was separated and refluxed gently for one-half hour with an equal volume of concd. sulfuric acid. The chloride was then distilled from the acid, washed with water, dried with calcium chloride and distilled. In the case of certain alcohols, the final distillation from sulfuric acid was not necessary because only a small amount of high-boiling material was formed. In Table I a statement is made when sulfuric acid was used.

In a number of cases a determination was made of the yield of chloride formed by refluxing the alcohol with hydrochloric acid without zinc chloride.

It is probable that the yields of chlorides would be greater if larger amounts of materials were used. The zinc chloride can be recovered for

TABLE I
PREPARATION OF ALKYL CHLORIDES

Alcohol	Ratio Alc.:HCl:ZnCl	Yield %	B. p. of chloride, °C.	Remarks
Methyl	1:2:2	79		Yield det. by vol.
Ethyl	1:2:2	60	12.5	Distilled through column without refluxing
<i>n</i> -Propyl	1:2:2	61	45-46	H ₂ SO ₄ used
	1:2:0	11		H ₂ SO ₄ not used
<i>i</i> -Propyl	1:2:2	76	35.5-37	H ₂ SO ₄ not used
	1:2:0	17	35.5-37	H ₂ SO ₄ not used
<i>n</i> -Butyl	1:2:2	65	76-78	H ₂ SO ₄ used
	1:2:0	8	76-78	H ₂ SO ₄ not used
<i>sec</i> -Butyl	1:2:2	78	66-68	Orig. product boiled at 62-70°; some tert. butyl chloride
	1:2:0	19		
<i>iso</i> -Butyl	1:2:2	4	69	Product boiled up to 225° H ₂ SO ₄ used
	1:2:1	15	69	H ₂ SO ₄ used
	1:2:0.5	0		
	1:2:2HgCl ₂	12	69	
	1:4:2CaCl ₂	0		
	1:2:2SnCl ₂	8	69	
	1:HCl(gas):2	0		
<i>iso</i> -Amyl	1:2:2	60	98.5-100	H ₂ SO ₄ used
	1:1:2	43	98.5-100	H ₂ SO ₄ used
	1:2:1	40	98.5-100	H ₂ SO ₄ used
	1:8:8	60	98.5-100	H ₂ SO ₄ used
	1:2:0	8	98.5-100	H ₂ SO ₄ used
Pentanol-2	1:2:2	75	95-97.5	Small amt. of low-boil. product
	1:2:0	57	95-97.5	Small amt. of low-boil. product
Cetyl	1:2:2	65	159-163 (2 mm.)	See Note 1 below
β -Phenylethyl	1:2:2	82	89-92 (16 mm.)	See Note 2 below
γ -Phenylethyl	1:2:2	40		See Note 3 below
<i>o</i> -Nitrobenzyl	1:2:2	trace		Decomposed
<i>m</i> -Nitrobenzyl	1:2:2	57	m. p. 45-47	See Note 4 below
<i>p</i> -Nitrobenzyl	1:2:2	67	m. p. 70-71	See Note 5 below

NOTE 1. One-twentieth mole of alc. used (12.1 g.). Product dissolved in ethyl alc.; 1.5 g. cetyl alc. crystallized. On evap., alc. sol. gave 12 cc. of oil. Seven cc. boiled at 159-163° (2 mm.) and melted at 13°.

NOTE 2. One-tenth mole of alc. used. Mixture heated to 65°. Reaction complete in 15 min. Chloride obt. free from alc. Did not change in vol. when treated with concd. HCl.

NOTE 3. One-twentieth mole used.

NOTE 4. Five g. of alc. used. Refluxed for 15 min. Upper layer solidified on cooling. Sep. and cryst. from ligroin.

NOTE 5. Five g. of alc. used. Dissolved when heated to 50°. Two layers formed at 100°. Product cryst. from ligroin.

further use by distilling the diluted acid from the mixture until it begins to "bump." To the residue are added the amounts of acid and alcohol previously used, and the process outlined above is repeated.

The results obtained are given in Table I.

Summary

1. The following alcohols are converted into chlorides when heated in an open vessel with concd. hydrochloric acid and zinc chloride: methyl, ethyl, *n*-propyl, *isopropyl*, *n*-butyl, *sec*-butyl, *isoamyl*, pentanol-2, cetyl, β -phenylethyl, γ -phenylpropyl, *m*-nitrobenzyl, *p*-nitrobenzyl.

2. The best results were obtained when the substances were used in the molecular ratio, 1 of alcohol, 2 of hydrogen chloride as concd. hydrochloric acid and 2 of zinc chloride. The yields varied from 60 to 82%.

3. The lower alkyl halides can be purified from high-boiling polymerization products by refluxing with concd. sulfuric acid.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

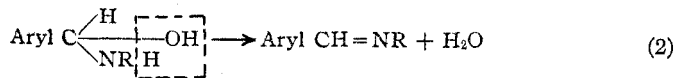
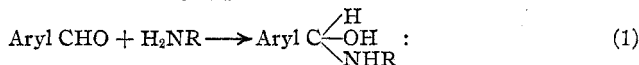
DERIVATIVES OF PARA-NITROBENZALDEHYDE. II

BY CHARLES G. KING¹ WITH ALEXANDER LOWY

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In a previous report² the object of the research and references to the literature were given.

The first series of reactions investigated was the preparation of "Schiff bases"³ according to the following type reactions.



In many cases the reaction is almost instantaneous, the whole mass becoming solid when the two reactants are mixed. It is often necessary, however, to select a suitable condensing medium and solvent, such as alcohol or glacial acetic acid. Heating the reacting materials together for some hours was found necessary to condense *p*-nitrobenzaldehyde with *o*-nitro-aniline, 2,6-dibromo-aniline and 2,4,6-tribromo-aniline. It is often impossible to isolate the intermediate addition compound, due to its instability or the speed of the second reaction. No compounds of the addition product type were isolated during this investigation.

¹ This report is the abstract of a thesis presented by Charles G. King in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1923.

² THIS JOURNAL, 43, 625 (1921).

³ Ber., 35, 984 (1902).