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Abstract

Full Text

Chemistry

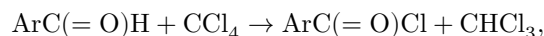
Yu. A. Ol' dekop, A. M. Kalinina, and S. A. Shklyar

A New Method for the Synthesis of Acid Chlorides and Acid Bromides of Aromatic Acids

(Presented by Academician M. I. Kabachnik, January 2, 1961)

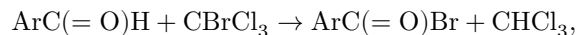
Among the relatively large number of methods for the synthesis of acid chlorides, there is a synthetic method based on the reaction between an aldehyde and a chlorinating agent. Thus, benzoyl chloride is obtained by the reaction of benzaldehyde with chlorine ⁽¹⁾, sulfuryl chloride ⁽²⁾, sulfuryl chloride ⁽³⁾, and ethyl hypochlorite ⁽⁴⁾. Among syntheses of preparative significance, the preparation of the acid chloride of *o*-chlorobenzoic acid from *o*-chlorobenzaldehyde and chlorine ⁽⁵⁾ should be noted.

In a brief publication by Winstein and Syubold ⁽⁶⁾, the reaction between isovaleric and β -phenylisovaleric aldehydes and carbon tetrachloride, proceeding in the presence of benzoyl peroxide, is described. As a result of the reaction, the acid chlorides of the corresponding acids were obtained in yields of 60 and 55%. Continuing investigations on the study of thermal reactions of CCl₄ ^(7,8), in the present work we report that CCl₄ reacts with aromatic aldehydes at 180–205° without the addition of peroxides and in this process forms acid chlorides in high yields (see Table 1)



where Ar = C₆H₅, p-CH₃C₆H₄, p-CH₃OC₆H₄, m-ClC₆H₄, p-ClC₆H₄, -C₁₀H₇.

Analogously to the reactions of carbon tetrachloride, the reactions of bromotrichloromethane with aldehydes proceed smoothly; in this case acid bromides are also formed in high yields



where Ar = C₆H₅, p-CH₃OC₆H₄.

The amount of chloroform (with both halides) usually corresponded to the amount of the acid halide obtained. Reactions between aromatic aldehydes and chloroform were not observed.

In the reaction of CCl_4 with *p*-methylbenzaldehyde, in addition to the main reaction, exchange of chlorine for hydrogen from the side chain occurred. The formation of hydrogen chloride and resins in the experiments was usually insignificant. On the contrary, resin formation was very great in the reaction of cinnamaldehyde and furfural with CCl_4 ; acid chlorides were absent from the reaction products. In the reaction with *m*- and *p*-nitrobenzaldehydes, formation of acid chlorides and chloroform likewise was not observed; formation of phosgene, hydrogen chloride, and resin was noted.

Carrying out the reaction of CCl_4 with benzaldehyde in an atmosphere of nitrogen greatly reduced the yield of benzoyl chloride; this makes it possible to conclude that traces of peroxides, usually formed in the interaction of aldehydes with oxygen, initiated the reaction. Introduction of inhibitors (hydro-

Table 1

Name of aldehyde	Temp., °C	Heating duration, h	Yield of CHCl_3 , %	Acid halide (yield, %)	B.p. of acid halide, °C (mm Hg)	n_D	M.p. of anilide, °C
Benzoic aldehydes*	200–205	12	91,9	Benzoyl chloride (93,9)	43 (2)	n_D^{20} 1,5535	162
<i>p</i> -Methylbenzoic	200–205	16	75,5	<i>p</i> -Methylbenzoyl chloride (58,0)	105–110 (10)	—	147–148
<i>p</i> -Methoxybenzoic	205–210	12	92,3	<i>p</i> -Methoxybenzoyl chloride (84,8)	105–107 (2)	n_D^{20} 1,5811	171

Name of aldehyde	Temp., °C	Heating duration, h	Yield of CHCl ₃ , %	Acid halide (yield, %)	B.p. of acid halide, °C (mm Hg)	n_D	M.p. of anilide, °C
<i>m</i> -Chlorobenzoic	200–205	18	78,2	<i>m</i> -Chlorobenzoyl chloride (77,9)	101–102 (12)	$n_D^{20,5}$ 1,5682	122–125
<i>p</i> -Chlorobenzoic	200–205	16	60,3	<i>p</i> -Chlorobenzoyl chloride (71,3)	103–104 (12)	n_D^{20} 1,5783	194
α -Naphthoic	180–185	11	71,1	α -Naphthoyl chloride (67,7)	128–131 (3)	n_D^{21} 1,6473	161
Reactions of CBrCl ₃ with aldehydes*	Reactions of CBrCl ₃ with aldehydes*	Reactions of CBrCl ₃ with aldehydes*	Reactions of CBrCl ₃ with aldehydes*	Reactions of CBrCl ₃ with aldehydes*	Reactions of CBrCl ₃ with aldehydes*	Reactions of CBrCl ₃ with aldehydes*	Reactions of CBrCl ₃ with aldehydes*
Benzoic	200–205	17	88,8	Benzoyl bromide (87,9)	55–59 (2)	n_D^{22} 1,5841	162
<i>p</i> -Methoxybenzoic	175–180	8	92,1	<i>p</i> -Methoxybenzoyl chloride (86,3)	147–153 (14)	n_D^{20} 1,6177	171

* Molar ratio of halide to aldehyde 5 : 1.

quinone, pyrocatechol) led to a slight decrease in the yield of benzoyl chloride and chloroform. The increase in this case in the relative amounts of chloroform, as compared with the acid chloride, indicates a reaction between CCl₄ and the inhibitors. The introduction of an inhibitor promoted resin formation.

The addition, in some cases, of cuprous chloride caused a slight increase in the yield of the acid chloride.

Experimental procedure

The experiments were carried out in thick-walled glass tubes, which were filled with a thoroughly purified reaction mixture, sealed, and heated in a Karius furnace. The reaction mixture was distilled on an efficient rectification column. The amount of chloroform was determined analogously¹. After distillation of the unreacted carbon tetrachloride (or bromotrichloromethane), the residue (the acid halide) was distilled under vacuum. The acid halide was identified by its boiling point and refractive index; in addition, the corresponding anilide was obtained.

Work in this direction is continuing.

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References cited

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

¹Yu. A. Oldekop, A. M. Kalinina, ZhOKh, **30**, 3358 (1960).