[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

RESEARCHES ON CHLORIMINES. III. THE DECOMPOSITION OF CERTAIN AROMATIC ALD-CHLORIMINES TO FORM NITRILES. A METHOD FOR THE PREPARATION OF NITRILES FROM ALDEHYDES[1]

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RECEIVED AUGUST 11, 1930 PUBLISHED NOVEMBER 5, 1930

The first two papers of this series[2] have described the preparation of a number of aromatic ald-chlorimines. It was shown that these compounds decomposed spontaneously at varying rates into hydrogen chloride and a nitrile. In the present investigation a number of ald-chlorimines have been decomposed with bases to form nitriles.

Although the early workers[3] observed that benzalchlorimine readily decomposes into benzonitrile and hydrogen chloride, Raschig,[4] was the only one who recorded a yield of the nitrile. He reported that a 40% yield of benzonitrile (calculated from benzaldehyde) was obtained by subjecting the impure condensation product of benzaldehyde and monochloramine to steam distillation in the presence of sodium hydroxide.

Since the isolation of a number of ald-chlorimines has now been accomplished, a rather simple yet greatly improved method has been developed for the preparation of certain nitriles. The chlorimines in cold alcoholic solution are treated with an alcoholic solution of either potassium hydroxide or sodium ethylate. The sodium or potassium halide is rapidly precipitated even at 0°, and in some cases almost quantitative yields of the nitriles are produced. Table I (Experimental Part) shows the actual yields of nitriles obtained from seven chlorimines. The reaction may be represented by the equation $RCH{=}NCl + KOH \longrightarrow RCN + KCl + H_2O$. This represents a good method for the preparation of nitriles from aldehydes since the latter are readily converted into chlorimines in good yields.

In view of the fact that an acetyl derivative of an ald-oxime is considered to have a *syn* configuration[5] when it yields a nitrile on treatment with alkali, it would appear that the ald-chlorimines described in this paper have *syn* configurations, since the latter readily yield nitriles in an analogous manner. However, as only one of the two possible stereoisomeric ald-chlorimines has been isolated in each case, it would be premature to assign a *syn* configu-

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[1] This paper is constructed from portions of a thesis presented by A. G. Gillaspie in partial fulfilment of the requirements for the degree of Master of Arts in the Graduate School of Arts and Sciences, Duke University.

[2] Hauser and Hauser, THIS JOURNAL, **52**, 2050 (1930); Hauser, Hauser and Gillaspie, *ibid.*, **52**, 4158 (1930).

[3] Luxmoore, *J. Chem. Soc.*, **69**, 191 (1896); Forster, *ibid.*, **107**, 265 (1915).

[4] Raschig, "Schwefel und Stickstoffstudien," **1924**, p. 80.

[5] See Cohn, "Organic Chemistry for Advanced Students," Part II, **1928**, p. 306.

ration to these compounds, for the other isomers if isolated might also be able to react with alkalies to form nitriles. Furthermore in cases where acetyl *anti* ald-oximes are hydrolyzed by alkalies to form oximes, the CH_3COO- group is replaced by hydroxyl, whereas chlorine attached to nitrogen in chloramines and other compounds[6] apparently is not hydrolyzed in this manner. Thus the decomposition of ald-chlorimines by alkalies to form nitriles does not necessarily indicate a *syn* configuration.

Although the decomposition of the chlorimine by the base was rapid in every case, it was plainly evident, by observing the rate of precipitation of the halide salt, that anisal- and piperonalchlorimines were decomposed at a lower rate than the other five compounds described in this paper. By analyses for active chlorine it was shown that *o*-chlorobenzalchlorimine was completely decomposed by sodium ethylate at 0° within one and one-half minutes, whereas anisalchlorimine was only 43% decomposed under similar conditions within two minutes, and not completely decomposed until after five minutes. This is rather significant since *o*-chlorobenzalchlorimine in the pure state is much more stable than anisalchlorimine. These observations suggest the study of the decomposition of ald-chlorimines by weaker bases such as amines, as here the reaction rate would doubtless be slow enough to measure more precisely. This work is now in progress.

Experimental

The ald-chlorimines used for the preparation of nitriles were prepared from aldehydes and monochloramine[7] according to the methods described in the first two papers of this series.[2] They were purified by recrystallization from alcohol and dried on a porous plate.

Preparation of Nitriles.—A sample (1.50 to 2.00 g.) of chlorimine is dissolved in the smallest possible amount of alcohol at room temperature and then cooled in an ice-bath. In cases where the chlorimine is sparingly soluble in alcohol a small quantity of acetone[8] will facilitate solution. To the cooled solution of the chlorimine is added a cold concentrated alcoholic solution of 1.25 equivalents of sodium ethylate or potassium hydroxide, and the mixture allowed to stand for several minutes or until the halide salt no longer precipitates. Sufficient cold water is then added to dissolve the halide salt and precipitate as much of the nitrile as possible. After filtering, more of the nitrile may be obtained by extracting the filtrate with small portions of ether, and evaporating the ether on a water-bath. The nitriles were dried in a vacuum desiccator, weighed and the yields calculated. The results are given in Table I. Several of the low yields could doubtless be increased if carried out on a large scale. After recrystallization from petroleum ether, the nitriles were identified by their melting points and by hydrolysis to the corresponding acids.

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[6] Sidgwick, "The Electronic Theory of Valency," 1927, p. 158.

[7] The method of preparation of monochloramine is described by Coleman and Hauser, THIS JOURNAL, 50, 1195 (1928). This is a modification of the method of Marckwald and Wille, *Ber.*, 56, 1319 (1923).

[8] Acetone solutions of the nitrochlorimines became deeply colored when treated with the base, and the crude nitriles obtained in these cases possessed a darker color than when only alcohol was used as solvent.

TABLE I

PERCENTAGE YIELDS OF NITRILES

	Base used			
	Sodium ethylate		Potassium hydroxide	
Chlorimine	(1)[a]	(2)[b]	(3)[a]	(4)[b]
Anisal-	81	94	77	95
o-Chlorobenzal-	73	85	70	83
Piperonal-	79	96	85	97
2-Chloro-5-nitrobenzal-	51	82		
p-Chlorobenzal-	47	60		
m-Nitrobenzal-	54	83		
o-Nitrobenzal-	60	70		

[a] Yields of nitrile obtained by precipitating with water only. [b] Total yields of nitrile obtained.

The yields of nitriles given in Table I were obtained from chlorimines which had been purified by recrystallization from alcohol. Excellent yields of good products have been obtained from several crude chlorimines when the latter were decomposed with sodium ethylate. Good yields of nitriles are obtained when calculated from the aldehydes, since yields of 80–85% of chlorimines calculated from aldehyde used are readily obtainable in most cases.

Rates of Decomposition of *o*-Chlorobenzalchlorimine and Anisalchlorimine.—Approximately 0.1 molar alcoholic solutions of the chlorimines in separate flasks were treated with slightly more than the calculated amount of sodium ethylate in alcoholic solution (1 *M*) at 0°. Samples were pipetted off and analyzed for active chlorine. *o*-Chlorobenzalchlorimine was completely decomposed within one and a half minutes, while anisalchlorimine was only 43% decomposed after two minutes and completely decomposed after five minutes.

Summary

A number of aromatic ald-chlorimines have been decomposed by sodium ethylate or potassium hydroxide in alcoholic solution to form good yields of nitriles. This represents a method for the preparation of nitriles from aldehydes, since the latter are readily converted into ald-chlorimines.

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