[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Researches on Chlorimines. IV. A Study of the Reactions of Certain Ald-chlorimines with Bases

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The purpose of this paper is to report the results of a preliminary study of the reactions of aromatic ald-chlorimines with bases leading to the formation of nitriles (1). This reaction evidently does not consist of the spontaneous decomposition of ald-chlorimines (2), followed by the neutralization of the hydrogen chloride that would be produced, for certain ald-chlorimines which are relatively stable react more rapidly with a base than do certain others which are thermally unstable.[1] Moreover, the rate of decomposition of an ald-chlorimine is greatly accelerated by alkali, although the reaction apparently is not reversible.[2] Hence, the base is an active agent in removing the hydrogen chloride.

$$\mathrm{RCH{=}NCl + B \longrightarrow RCN + B{\cdot}H^+ + Cl^-} \tag{1}$$

$$\mathrm{RCH{=}NCl \longrightarrow RCN + HCl} \tag{2}$$

It should be of interest to determine the relative ease of removal of hydrogen chloride from ald-chlorimines by bases, since there is a possibility of correlating these data with the ionization constants of the corresponding acids and phenols. For this work we have chosen *o*-nitro-, *m*-nitro, *p*-chloro- and *p*-methoxy-benzalchlorimines, as they were readily available, and because their corresponding acids and phenols possessed ionization constants which differed from one another to an appreciable degree. Their relative rates of reaction have been determined with alkali in 95.6% alcohol, and with isoamylamine in benzene solution. Also, we have determined the relative rates of reaction of five different bases with *m*-nitrobenzalchlorimine in benzene solution.

Experimental

Solvents and Reagents.—Kahlbaum benzene was dried for a week over phosphorus pentoxide and then carefully fractionated through a 1.8-meter column. The middle fraction boiling at 79.9 ± 0.1° was used.

Eastman isoamylamine was dried for a week over solid potassium hydroxide and then decanted and distilled through a four-bulb column. The middle fraction distilling at 96.6 ± 0.1° was used. Eastman piperidine, benzylamine, acetamide and triphenylamine were used without further purification. Alcoholic alkali solution (0.04 *M*) was prepared from sodium and 95.6% alcohol.

Ald-chlorimines.—The ald-chlorimines used in this work were prepared from the corresponding aldehydes and monochloramine and recrystallized from cold dilute

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[1] (a) Hauser, Hauser and Gillaspie, THIS JOURNAL, **52**, 4163 (1930); (b) Hauser and Gillaspie, *ibid.*, **52**, 4518 (1930).

[2] Nitriles add hydrogen chloride to form imido chlorides (RCCl=NH) or nitrile hydrochlorides (RCN·HCl), Hantzsch, *Ber.*, **64B**, 667 (1931); see also Stephen, *J. Chem. Soc.*, **127**, 1874 (1925). Mr. A. E. Rainsford has shown in this Laboratory that when hydrochloric acid is added to an alcoholic solution of *p*-chlorobenzonitrile in an atmosphere of carbon dioxide, no test for active chloride is obtained.

alcohol by methods described previously.[1] The products were pressed on porous plates until essentially dry and then kept over potassium hydroxide in desiccators at 5° for several hours. Special care was taken to dry thoroughly the samples that were used in the work with benzene solutions. Certain of the chlorimines used in this work gave analytical figures for active chlorine which were practically identical with the theoretical values, and all of the products were at least 99% pure.

Reaction of Ald-chlorimines with Bases.—Previously,[1b] yields of nitriles as high as 96% of the theoretical quantities have been isolated from the reaction products of ald-chlorimines and alkali. When *p*-methoxybenzalchlorimine in alcoholic solution was decomposed by alkali, the product obtained after removing the alcohol and washing with water was practically pure nitrile (m. p. 57°). Tests for aldehydes were negative.

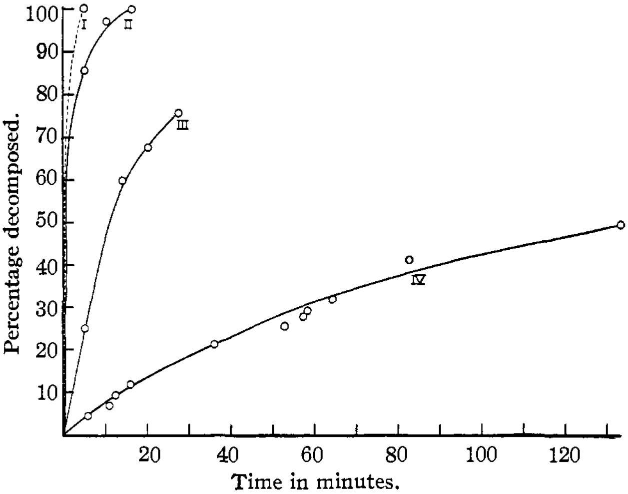

Fig. 1.—Relative rates of reaction of 0.01 *M* substituted benzalchlorimines with 0.02 *M* alkali in 95.6% alcoholic solution at 0°: I, *o*-nitro-; II, *m*-nitro-; III, *p*-chloro-; IV, *p*-methoxy-.

It has been shown in the following manner that ald-chlorimines neutralize equivalent molecular quantities of alkali. Alcoholic solutions of the chlorimines were mixed with excess of standard alkali. After tests for active chlorine were negative, the excess base was titrated with standard acid, using phenolphthalein as indicator. The data are given in Table I. The *o*- and *m*-nitrobenzalchlorimines were completely decomposed at 0° within a few minutes (see Fig. 1). Since the *p*-chloro and *p*-methoxy compounds were allowed to stand with the base at room temperature for several hours, blanks were run with the corresponding nitriles and alkali. The nitriles caused the neutralization of less than 2% of the alkali.

TABLE I

Calcd. 100 cc. 0.01 *M* $o\text{-NO}_2\text{C}_6\text{H}_4\text{CH{=}NCl}$	= 10.00 cc. 0.1 *N* NaOH.	Found:	9.96 cc.
Calcd. 100 cc. 0.01 *M* $m\text{-NO}_2\text{C}_6\text{H}_4\text{CH{=}NCl}$	= 10.00 cc. 0.1 *N* NaOH.	Found:	10.04 cc.
Calcd. 0.3046 g. $p\text{-ClC}_6\text{H}_4\text{CH{=}NCl}$	= 17.51 cc. 0.1 *N* NaOH.	Found:	17.57 cc.
Calcd. 0.3172 g. $p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH{=}NCl}$	= 18.71 cc. 0.1 *N* NaOH.	Found:	18.68 cc.

It has been shown that ald-chlorimines react with amines in benzene solutions according to the equation $\text{RCH{=}NCl} + \text{R'NH}_2 \longrightarrow \text{RCN} + \text{R'NH}_2\cdot\text{HCl}$. The amine hydrochloride precipitated as white crystals from benzene solution in yields generally more than 90% of the theoretical quantities. After removing the excess amine by means of acid, the nitrile was obtained by evaporating the solvent. With *o*-nitrobenzalchlorimine and isoamylamine in benzene solution, a yield of nitrile corresponding to 90% of the theoretical quantity was obtained. However, with less reactive ald-chlorimines, impure products were obtained from which smaller yields of pure nitriles were isolated.

Rates of Reaction.—Equal volumes of 0.04 *M* alkali and 0.02 *M* ald-chlorimine solutions in 95.6% alcohol were mixed and kept at 0 ± 1°. At intervals samples were run into a mixture of acetic acid and potassium iodide solution, and titrated with standard thiosulfate, adding water near the end of the titration in order to obtain a starch-iodide end-point. It was shown that the ald-chlorimines were stable in neutral alcoholic solutions for several hours. In the general procedure for the reactions in benzene solution 5-cc. samples of 0.4 *M* amine and 0.2 *M* ald-chlorimine solutions were mixed in test-tubes and kept at 30 ± 0.1°. At intervals the contents of the tubes were shaken with a mixture of 5 cc. of acetic acid, 5 cc. of 50% potassium iodide solution and 10 cc. of alcohol and titrated with thiosulfate. Difficulty was encountered in these analyses of benzene solutions of the chlorimines. However, the results with isoamylamine could usually be checked within ±5% during the first half of the decompositions. The rate of decomposition of *m*-nitrobenzalchlorimine in 0.1 *M* benzene solution was measured as a blank.

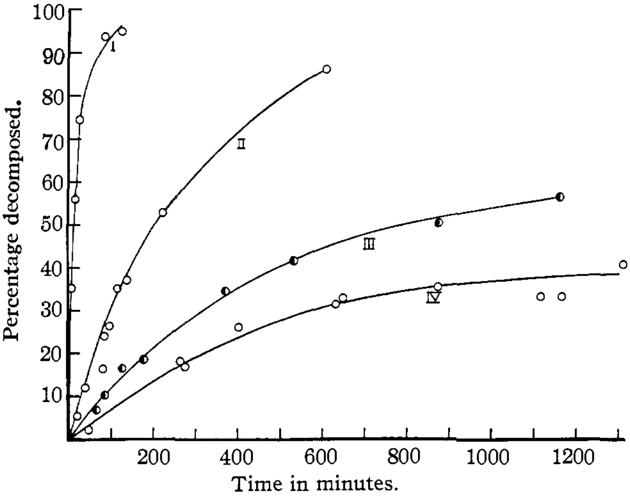

Fig. 2.—Relative rates of reaction of 0.1 *M* substituted benzalchlorimines with 0.2 *M* isoamylamine in benzene solutions at 30°: I, *o*-nitro-; II, *m*-nitro-; III, *p*-chloro-; IV, *p*-methoxy-.

The percentage chlorimine decomposed has been plotted against the corresponding time in Figs. 1, 2 and 3. In Fig. 3 the approximate ionization constants of the three strongest bases are also given. For comparison, the results for acetamide, triphenylamine and the blank are plotted on the same diagram using a different time scale. Their experimentally determined results can be obtained by multiplying the values given for the time by ten. Due to the limited solubility of acetamide in benzene its concentration was two-thirds that of the other bases. After periods of thirty and forty-five days the percentage decompositions of the blank were 25 and 50%, whereas those of the chlorimine in the presence of triphenylamine were 13 and 22%, respectively. Although the products of decomposition of the chlorimine evidently accelerated its further decomposition in both cases, the chlorimine was apparently more stable in the presence of the triphenylamine.

***p,p'*-Dichlorobenzophenone Chlorimine**[3] **with Bases.**—This keto-chlorimine was allowed to react with alkali in alcoholic solution, and with isoamylamine in benzene solution under conditions similar to those used in the work with ald-chlorimines described above. After periods of one and one-half and thirty hours the active chlorine content of an alcoholic solution of 0.01 *M* chlorimine with 0.02 *M* alkali at 0° was decreased to the extent of 0.5 and 3.5%, respectively. When the alcohol was evaporated on a water bath a product was obtained which was identified as *p,p'*-dichlorobenzophenone.

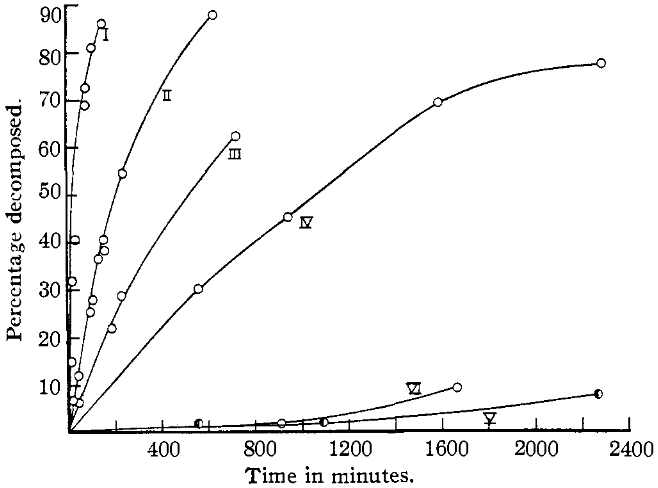

Fig. 3.—Relative rates of reaction of 0.2 *M* bases with *m*-nitrobenzalchlorimine in benzene solution at 30° : I, piperidine, $K_B = 1.3 \times 10^{-3}$; II, isoamylamine, $K_B = 4 \times 10^{-4}$; III, benzylamine, $K_B = 2 \times 10^{-5}$; IV, acetamide (multiply time scale by ten); V, blank (multiply time scale by ten); VI, triphenylamine (multiply time scale by ten).

The keto-chlorimine (0.1 *M*) with isoamylamine (0.2 *M*) in benzene solution at 30° was 2% decomposed after nineteen hours and 10% after six days.

TABLE II

IONIZATION CONSTANTS OF ACIDS, PHENOLS AND ANILINES CORRESPONDING TO SUBSTITUTED BENZALCHLORIMINES

Benzalchlorimines	*o*-Nitro-	*m*-Nitro-	*p*-Chloro-	*p*-Methoxy-
Acids K_A	6×10^{-3}	3×10^{-4}	9.1×10^{-5}	3.3×10^{-5}
Phenols K_A	5.6×10^{-8}	5×10^{-9}	4×10^{-10}	....
Anilines K_B	1.5×10^{-14}	3.2×10^{-12}	1.2×10^{-11}	5.7×10^{-9}

Discussion of Results

Evidence is presented in the experimental part which indicates that the reaction of 0.02 *M* alkali with 0.01 *M* ald-chlorimine[4] in alcoholic solution

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[3] Hauser and Humble, THIS JOURNAL, **54**, 2476 (1932).

[4] Bimolecular constants calculated for 10 to 50% decomposition of *p*-methoxybenzalchlorimine agreed within ±5%. The average value was 0.285.

(Fig. 1) proceeded quantitatively according to equation (1). The predominant reaction of 0.2 *M* isoamylamine with 0.1 *M* ald-chlorimine in benzene solution (Fig. 2) also can be represented by equation (1). It is probable that the extent of side reaction which occurred under these conditions was less than 2% during the first half of the decompositions of the ald-chlorimines, since, in an interval of nineteen hours, *p,p'*-dichlorobenzophenone chlorimine was only 2% decomposed, whereas the corresponding ald-chlorimine was 55% decomposed under similar conditions. The results in Figs. 1, 2 and 3 are considered to represent merely the relative rates of reactions of these ald-chlorimines with bases.

It is evident from Figs. 1 and 2 and Table II that the relative ease of removal of hydrogen chloride from *o*-nitro-, *m*-nitro, *p*-chloro- and *p*-methoxy-benzalchlorimines by means of alkali in alcoholic solution, and by means of isoamylamine in benzene solution, is in the same relative order as the ionization constants of the corresponding acids and phenols, and in the inverse order to those of the corresponding substituted anilines. It can be seen from Fig. 3 that the relative rates of reaction of various amines with *m*-nitrobenzalchlorimine in benzene solution are in the same relative order as the ionization constants of the bases.[5]

The writers believe that the most plausible mechanism for the removal of hydrogen chloride consists of the withdrawal of a proton* from the ald-chlorimines ($RCH^*{=}NCl$) under the influence of the base, followed by the removal of the chloride ion. The fact that keto-chlorimines ($RCR{=}NCl$) do not react with bases in this manner indicates that the removal of the chloride ion from an ald-chlorimine to form a nitrile depends upon the presence of the aldehydic hydrogen. It is possible therefore to regard the relative rates of reaction of the various ald-chlorimines with a base as a measure of the relative reactivities of the aldehydic hydrogen of these ald-chlorimines.

Summary

It has been shown that the relative ease of removal of hydrogen chloride from *o*-nitro-, *m*-nitro-, *p*-chloro- and *p*-methoxy-benzalchlorimines by means of alkali in alcoholic solution, and by means of isoamylamine in benzene solution, are in the same relative order as the ionization constants of the corresponding acids and phenols. It was shown also that the relative rates of reaction of various amines with *m*-nitrobenzalchlorimine in benzene solution are in the same relative order as the ionization constants of the bases.

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(5) Since these ionization constants have been determined in water, only a qualitative relationship was expected between these constants and the rates of reaction of the bases with the ald-chlorimine in benzene solution. The rate for acetamide, however, was much faster than would be expected from its basic strength.