as a white indistinctly crystalline powder. It was filtered off and allowed to stand in a vacuum over sulfuric acid overnight, when it changed to a thick sirup. This was dissolved in water and reprecipitated with alcohol. The precipitate was allowed to remain in contact with the mother liquor for two days, then filtered off and dried at 40° in air. The barium salt was obtained as a white chalky powder.

Anal. Subs., 0.1540, 0.1681: $BaSO_4$, 0.0943, 0.1034. Calcd. for $C_6H_8O_6S_2Ba$: Ba, 36.34. Found: Ba, 36.03, 36.19.

β,β'-Dithiodiglyceric Acid, $(—SCH_2CHOHCOOH)_2$.—A solution of 3.77 g. of the barium salt in water was treated with the calculated amount of *N* sulfuric acid. The barium sulfate was filtered off and the resulting solution was evaporated to a sirup on a water-bath. After this sirup had stood over sulfuric acid in a vacuum for several days, a thick gum remained, weighing 2.30 g. (calcd., 2.42 g.).

Anal. Subs., 0.1397: $BaSO_4$, 0.2676. Calcd. for $C_6H_{10}O_6S_2$: S, 26.45 Found: S, 26.31.

The acid was easily soluble in water and in ethyl acetate; it was precipitated from its solution in the latter solvent by chloroform as a sticky gum.

The writer wishes to express his appreciation of the assistance and advice offered by Professor S. M. McElvain.

Summary

1. A new method of preparation of β-chlorolactic acid has been described.

2. β-Thioglyceric acid and a few of its derivatives have been prepared from ethyl β-chlorolactate.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY AND THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

THE PREPARATION OF PRIMARY AMINES FROM ALDEHYDES AND MONOCHLORO-AMINE

BY CHARLES R. HAUSER

RECEIVED SEPTEMBER 30, 1929 PUBLISHED MARCH 6, 1930

In view of the fact that oximes have been reduced to primary amines, it would seem possible that chloro-imines could be reduced in a similar manner. Thus primary amines might be prepared from aldehydes and monochloro-amine by the reduction of the intermediate chloro-imine, as represented by the equation

$$RCH{=}O + H_2NCl \xrightarrow{-H_2O} RCH{=}NCl \xrightarrow{+\,4H} RCH_2NH_2HCl$$

With the exception of methylene chloro-imine,[1] apparently no chloro-imine prepared by this method has been isolated. However, there is evidence that benzalchloro-imine is the condensation product of benzaldehyde and monochloro-amine. Forster[2] reported that benzonitrile and

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[1] Cross, Bevan and Bacon, *J. Chem. Soc.*, **97**, 2404 (1910).

[2] Forster, *ibid.*, **107**, 265 (1915).

ammonium chloride are obtained when an ether solution of the supposed benzalchloro-imine is evaporated on a water-bath. Raschig[3] was unsuccessful in his attempt to purify the condensation product of benzaldehyde and monochloro-amine. His analysis of the crude product for active chlorine gave 80–85% of benzalchloro-imine. When heated with water or sodium hydroxide solution the condensation product decomposed into hydrogen chloride and benzonitrile.

In the present investigation no attempt was made to isolate the chloro-imines, as it seemed that these would be unstable in view of the fact that Luxmoore[4] has reported that pure benzalchloro-imine decomposes even at 0°. However, good yields of primary amines were obtained from certain aldehydes and monochloro-amine by reducing the intermediate chloro-imine in alcoholic solution with sodium amalgam. Further work on chloro-imines is being carried out.

Experimental

In a preliminary experiment further evidence was obtained that the condensation product of benzaldehyde and monochloro-amine is doubtless benzalchloro-imine. As would be expected[5] dry hydrogen chloride reacts with an ether or carbon tetrachloride solution of the condensation product according to the equation

$$\mathrm{RCH{=}NCl + 2HCl \longrightarrow RCH{=}NH{\cdot}HCl + Cl_2}$$

The imine hydrochloride obtained as a white precipitate is readily hydrolyzed into benzaldehyde and ammonium chloride which were identified.

Monochloro-amine[6] in cold aqueous solution was condensed with three aromatic and two aliphatic aldehydes by a modification of the methods of Forster[2] and Raschig.[3] The crude condensation product was dissolved in alcohol and reduced with sodium amalgam by an adaptation of the method used by Goldschmidt[7] for the reduction of oximes. The results obtained with the aromatic aldehydes are given in Table I. The products obtained as amine hydrochlorides were analyzed and derivatives prepared.

Benzaldehyde and *p*-tolualdehyde gave yellow liquid condensation products doubtless mixed with some unchanged aldehyde, while *o*-chlorobenzaldehyde gave a white solid which melted to an oil at about 15–20°. Analysis of the latter condensation product for the active chlorine showed that it was 90.2% pure calculated as the chloro-imine.

From each of the chloro-imines of benzaldehyde and *o*-chlorobenzaldehyde there

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[3] Raschig, "Schwefel- und Stickstoffstudien," **1924**, p. 78.

[4] Luxmoore, *J. Chem. Soc.*, **69**, 191 (1896).

[5] Hydrogen chloride reacts with keto-chloro-imines to form the imine hydrochloride, Stieglitz and Peterson, *Ber.*, **43**, 786 (1910).

[6] Monochloro-amine was prepared by the method of Coleman and Hauser, THIS JOURNAL, **50**, 1193 (1928). This is a modification of the method of Marckwald and Wille, *Ber.*, **56**, 1319 (1923).

[7] Goldschmidt, *ibid.*, **19**, 3232 (1886).

TABLE I

PERCENTAGE YIELDS

Aldehyde	Condensation product[a]	Amines (1)[b]	Amines (2)[c]
p-$CH_3C_6H_4CHO$	69.0	63.6	43.8
C_6H_5CHO	70.2	73.5	51.5
o-ClC_6H_4CHO	87.7	77.0	67.5

[a] Yields of crude condensation products calculated from aldehydes. [b] Yields of primary amines calculated from crude condensation products. [c] Yields of primary amines calculated from aldehydes.

was obtained a yield of approximately 85% of primary amine calculated from the active chlorine content of the crude condensation product.

Two aliphatic aldehydes, *n*-propionaldehyde and *n*-butyraldehyde, gave with monochloro-amine fair yields of very unstable yellow liquids, which were assumed to be the crude chloro-imines. Since the reduction of these chloro-imines gave very small yields of amines, they were not studied farther in the present work.

Condensation of Aldehydes with Monochloro-amine.—The aldehyde was thoroughly shaken with excess of an ice-cold aqueous solution of monochloro-amine[6] prepared from equal volumes of normal solutions of sodium hypochlorite and ammonium hydroxide. Benzaldehyde, and likewise *p*-tolualdehyde, with monochloro-amine produced a milky mixture which was allowed to stand in an ice chest until the condensation product had settled to the bottom as a yellow oil. The condensation product was then separated, a weighed amount dissolved in alcohol and reduced as described below. A milky mixture was at first produced from *o*-chlorobenzaldehyde and monochloro-amine, but after shaking for about fifteen minutes a white precipitate formed. The precipitate was filtered off at a low temperature and a weighed amount dissolved in alcohol and reduced. In these reactions sufficient monochloro-amine solution was always used to have its odor persist until the condensation product was separated from the aqueous solution.

Reduction.—Approximately twice the theoretical amount of sodium amalgam (2.5%) was added in small portions to a solution of 2 g. of the crude condensation product in 25 cc. of alcohol and 12 cc. of glacial acetic acid. The reaction mixture was kept below 35°. More alcohol was added if a heavy precipitate formed. When the reaction was complete three volumes of water were added, and after separating the mercury the cooled solution was made alkaline. The aqueous solution of amine was extracted three times with ether and the ether solution extracted with dilute hydrochloric acid. The amine hydrochloride, obtained by evaporating the hydrochloric acid solution on a water-bath, was dried thoroughly in a vacuum desiccator.

The purity of the amine hydrochlorides was determined by analysis and the amines were identified by preparing derivatives and taking mixed melting points when known compounds were available.

Anal. Calcd. for $C_8H_{11}N{\cdot}HCl$: N, 8.89; HCl, 23.16. Found: N, 8.77; HCl, 23.20.

Anal. Calcd. for $C_7H_9N{\cdot}HCl$: N, 9.76; HCl, 25.51. Found: N, 9.89; HCl, 25.15.

Anal. Calcd. for $C_7H_8NCl{\cdot}HCl$: N, 7.87; HCl, 20.50. Found: N, 7.86; HCl, 20.40.

Several reductions of benzalchloro-imine were carried out at temperatures ranging from 0 to 40° and it was found that below 35° approximately the same yields of amines were obtained. A smaller yield was obtained when the reaction was carried out at 30–40° by adding the acetic acid slowly so that the solution was always slightly acidic.

Summary

A method for the preparation of certain primary amines is described in which monochloro-amine is condensed with an aldehyde and the condensation product in alcoholic solution reduced with sodium amalgam.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE THERMAL DECOMPOSITION OF METAL ALKYLS IN HYDROGEN-ETHYLENE MIXTURES

BY HUGH S. TAYLOR AND WILLIAM H. JONES

RECEIVED OCTOBER 1, 1929 PUBLISHED MARCH 6, 1930

The reactivity of metal alkyls undergoing decomposition by heat offers many interesting problems of both scientific and practical interest. The production of a reactive fragment of decomposition among inert hydrocarbons might offer a means of bringing these compounds into a state of reactivity with the possible formation of more interesting products. A study of the reactivity of such fragments with hydrogen is of importance also as indicating the direction of chemical change in systems obtaining when hydrocarbons are subjected to processes of thermal degradation or "cracking." To these ends we have investigated the decomposition of several metal alkyls in the presence of various mixtures of hydrogen and ethylene.

When a metal alkyl is decomposed by heat, leaving the free metal as a deposit, it seems an unavoidable assumption that the alkyl group must have existed, at least for a short space of time, as a free radical. If it can then be shown that any resulting reaction could not be attributed to the metal or to the temperature, the postulated mechanism of whatever reaction occurs must be such as to involve the alkyl radical. For this reason mercury diethyl and lead tetraethyl were chosen, since they decompose under temperature conditions which do not of themselves induce reaction of hydrogen and ethylene, and since the metals themselves do not exhibit any marked catalytic effect.

Extensive recent work by Taylor and Marshall,[1] Olson and Meyers,[2] Bates and Taylor,[3] Taylor and Hill,[4] Bonhoeffer and Harteck,[5] von Wartenburg and Schultze,[6] and others demonstrates the interest which atomic

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[1] Taylor and Marshall, *J. Phys. Chem.*, **29**, 1140 (1925).

[2] Olson and Meyers, THIS JOURNAL, **48**, 389 (1926).

[3] Bates and Taylor, *ibid.*, **49**, 2438 (1927).

[4] Taylor and Hill (Taylor, "Nichols Medal Address"), *Ind. Eng. Chem.*, **20**, 439 (1928); THIS JOURNAL, **51**, 2922 (1929).

[5] Bonhoeffer and Harteck, *Z. physik. Chem.*, **139A**, 64 (1928).

[6] Von Wartenburg and Schultze, *ibid.*, **2B**, 1 (1929).