rial behaved in a manner analogous to the product synthesized by Kühn and Stein.

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The Reduction of Certain Halogenated Nitroparaffins by Liquid Ammonia. II. Brompicrin

BY EDWARD SCHULZ, SEYMOUR MEISEL AND FREDERIC C. SCHMIDT

Schmidt, Sunderlin and Cole[1] showed that dibromodinitromethane, dichlorodinitromethane and chlorobromodinitromethane are reduced by anhydrous ammonia at its boiling point with the loss of a halogen according to the general equation

$$3X_2C(NO_2)_2 + 8NH_3 \longrightarrow 3XC(NO_2)_2NH_4 + 3NH_4X + N_2$$

When bromochlorodinitromethane was used, it was the bromine which was removed.

Hsing-Han Liu and Peter P. T. Sah[2] attempted to prepare guanidine from tribromonitromethane and alcoholic ammonia, but reported that the reaction mixture exploded.

This investigation shows the reaction of tribromonitromethane (brompicrin) with anhydrous liquid ammonia and a possible mechanism for the reaction.

Experimental

Preparation of Materials. Brompicrin.—Brompicrin was obtained from Eastman Kodak Co. and steam distilled. The product was dried over anhydrous sodium sulfate, vacuum distilled and collected over a temperature range of 85–87° (16 mm.); d^{20}_4 2.7880; n_D 1.5790; m.p. 10.2–10.3°.

Dibromomononitromethane.—The method of Scholl was used except in the purification of the material. The dibromonitromethane obtained reacted with anhydrous liquid ammonia to give the ammonia salt. The salt was dissolved in distilled water, reforming the dibromonitromethane by the addition of an excess of hydrobromic acid; b.p. 53–54° at 17 mm. pressure; d^{20}_4 2.3846; n_D 1.528.

Reaction of Brompicrin with Anhydrous Liquid Ammonia.—A fragile bulb filled with a weighed amount of brompicrin was placed in a reaction vessel which was kept at −33° by a dewar filled with liquid ammonia. The vessel was evacuated, and about 50 ml. of liquid ammonia was distilled into it. The bulb was broken by means of a plunger. A violent reaction occurred between the brompicrin and the ammonia accompanied by a colorless inert gas. The evolved gas was washed free from ammonia and dried overnight over phosphorus pentoxide. After drying, the gas was drawn into an evacuated flask of known volume and the density determined. The molecular weight of the contained inert gas was calculated to be 28; 28.5 for two different determinations. This is in excellent agreement with the molecular weight of nitrogen, 28. The ratio of the moles of brompicrin to moles of nitrogen formed is given in Table I.

TABLE I

QUANTITATIVE REDUCTION OF BROMPICRIN

Grams	Moles $\times 10^{-3}$	N_2 liberated moles $\times 10^{-3}$	$BrC(NO_3)/N_2$
1.4214	4.77	1.62	2.94:1
2.2549	7.85	2.49	3.05:1

After the nitrogen had been completely evolved, the excess liquid ammonia was allowed to evaporate leaving a bright yellow solid. This solid, suspected of being a mixture of the ammonium salt of dibromonitromethane and ammonium bromide, was treated with an excess of aqueous HBr. The heavy oil which separated was washed with water, dried and vacuum distilled: d^{20}_4 2.3845; n_D 1.528. These physical constants are identical with those of dibromonitromethane. The infrared spectrum of this oil was compared to that of known dibromonitromethane and they were found identical.

The other solid, beside the ammonium salt of dibromonitromethane, was shown by analysis to be ammonium bromide in equal molar quantities.

Discussion of Results.—The evidence of Table I along with the infrared spectra determinations, density and index of refraction measurements indicates without doubt that the reaction between brompicrin and anhydrous liquid ammonia proceeds according to the equation

$$3Br_3CNO_2 + 8NH_3 \longrightarrow 3BrCNO_2NH_4 + 3NH_4Br + N_2$$

This equation is similar to that found by Schmidt, Sunderlin and Cole[1] for dibromodinitromethane.

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[1] Schmidt, Sunderlin and Cole, *J. Org. Chem.*, **9**, 419 (1944).

[2] Hsing-Han Liu and Peter P. T. Sah, Science Reports, National Tsinghua University, A_2 129-B1 (1933).

A New Synthesis of Glyoxal Tetramethyl Acetal

BY RALPH C. SCHREYER

Glyoxal tetramethyl acetal has been prepared from glyoxal sulfate and methanol[1] or glyoxal sulfate, methanol and calcium chloride.[2] Acetals of glyoxal have also been synthesized from aqueous glyoxal and alcohols.[3]

Recently in this Laboratory the preparation of glyoxal tetramethyl acetal has been accomplished by the addition of chlorine to 1,2-dimethoxyethylene[4] followed by reaction with methanol.

$$CH_3OCH{=}CHOCH_3 + Cl_2 \longrightarrow CH_3OCHClCHClOCH_3$$
$$+ 2CH_3OH \longrightarrow (CH_3O)_2CHCH(OCH_3)_2 + 2HCl$$

Attempts to isolate the chlorine addition product by vacuum distillation were unsuccessful because of dehydrochlorination of the reactive bis-chloroether.

In most cases, it was desirable to add some sodium methoxide after the reaction with methanol in order to drive the reaction to completion and to remove all traces of hydrogen chloride. Higher yields would probably be attained if a stoichiometric amount of sodium methoxide were employed instead of using methanol. This synthesis should be applicable to other 1,2-dialkyloxyethylenes, allowing the synthesis of other acetals or mixed acetals of glyoxal.

Experimental

Glyoxal Tetramethyl Acetal.—Chlorine (24 g., 0.34 mole) was added slowly over a 15-minute period to 30 g. (0.34 mole) of 1,2-dimethoxyethylene stirred at 0°. A white solid separated out from the reaction mixture. Methanol (22 g., 0.69 mole) was then added at 0° and the resulting solution was heated to 60° until the evolution of hydrogen chloride ceased (time about one-half hour). Vacuum dis-

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[1] H. O. L. Fischer and C. Taube, *Ber.*, **59B**, 851 (1926).

[2] D. H. Grangaard and C. B. Purves, THIS JOURNAL, **61**, 428 (1939).

[3] L. G. MacDowell and R. W. McNamee, U. S. Patent 2,321,094 (1943); U. S. Patent 2,360,959 (1944).

[4] Dimethoxyethylene is prepared by the demethanolation of 1,1,2-trimethoxyethane, W. F. Gresham, U. S. Patent 2,479,068; 1,1,2-trimethoxyethane is synthesized from (1) carbon monoxide, hydrogen, methanol and methylal using a cobalt catalyst, W. F. Gresham and R. E. Brooks, U. S. Patent 2,449,470, or (2) methanol and methoxyacetaldehyde.