ethanol, and this ethanol wash was combined with the original reaction filtrate. An ethanol solution of picric acid was added to these combined solutions and two crystalline picrates were obtained. The first picrate, weighing 12.9 g., was removed and upon examination proved to be a mixture of potassium picrate and the dipicrate of 1,3-diaminopropanol. The second picrate, which weighed 3.16 g., was extracted with ether to remove residual picric acid and recrystallized from ethanol. Three crops were obtained. The second and third crops were combined and recrystallized from ethanol; care was taken not to dissolve all the solid in the ethanol (about 0.2 g.). A picrate was obtained which melted at 179–185° (2.0 g., 10.5% calculated as 5-hydroxy-2-imino-1,3-diazacyclohexane picrate). After recrystallization from ethanol the compound melted at 182–185°. A mixed melting point with an authentic sample of 5-hydroxy-2-imino-1,3-diazacyclohexane picrate was not depressed. The combined first crops and insolubles were processed and an additional 1.5% of the imino compound was isolated.

1-Amino-3-guanidinopropanol dihydrochloride. 1,3-Diaminopropanol (25.1 g., 0.278 mole) was dissolved in 35 ml. of ethanol, heated to 40° and stirred while 56.2 g. (0.368 mole, 32% excess) of 2-methyl-2-thiopseudourea nitrate dissolved in 35 ml. of warm water was added over a period of 40 min. After the addition was complete, the reaction mixture was maintained at 40° for an additional 15 min., then cooled, filtered, and the precipitate washed with ethanol. The filtrate was added to an excess of an aqueous picric acid solution and the picrate formed, after extraction with ether and hot methanol, weighed 39.0 g. These salts, after conversion to hydrochloride salts, weighed 10.2 g. (17.9%) and melted at 145–150°. Recrystallization from ethanol gave a product which melted at 154.5–155.5°.

Anal. Calcd. for $C_4H_{14}Cl_2N_4O$: C, 23.42; H, 6.88; Cl, 34.58; N, 27.32. Found: C, 23.42; H, 6.55; Cl, 34.28; N, 27.37.

1-Amino-3-guanidinopropane dihydrochloride. This salt was prepared in the same manner as 1-amino-3-guanidinopropanol. However, a somewhat smaller excess of 2-methyl-2-thiopseudourea nitrate can be used since the dihydrochloride salt of 1,3-diaminopropane separates readily from the dihydrochloride salt of 1-amino-3-guanidinopropane when the hydrochloric acid solution is allowed to evaporate. After crystallization from absolute ethanol and then from an ethanol-benzene solution, the product melted at 156–157°.

Anal. Calcd. for $C_4H_{14}Cl_2N_4$: C, 25.41; H, 7.46; Cl, 37.50; N, 29.63. Found: C, 25.41; H, 7.68; Cl, 37.90; N, 29.69.

Cyclization of 1-amino-3-guanidinopropanol. A. 1-Amino-3-guanidinopropanol dihydrochloride (0.3 g., 0.00146 mole) was added to 15 ml. of water and refluxed 3 hr. An excess of an aqueous picric acid solution was then added, and the precipitate which formed was collected and extracted with ether. A mixed melting point with an authentic sample of 1-amino-3-guanidinopropanol dipicrate was not depressed.

B. 1-Amino-3-guanidinopropanol dihydrochloride (0.28 g., 0.00139 mole) was added to 15 ml. of water containing 0.00138 mole of sodium hydroxide and refluxed for 2 hr. An excess of an aqueous solution of picric acid was added, and the precipitate after extraction with ether melted at 185–186° and weighed 0.25 g. (52%). A mixed melting point with an authentic sample of 5-hydroxy-2-imino-1,3-diazacyclohexane picrate was not depressed.

2-Imino-1,3-diazacycloalkane salts. The corresponding diamine (0.04 mole) was dissolved in 10 ml. of water in a flask equipped with a reflux condenser and stirrer. The diamine solution was heated to reflux and 0.04 mole of the nitrate salt of 2-methyl-2-thiopseudourea, dissolved in 25 ml. of water, was added over a period of 40 min. After the addition was complete, the reaction mixture was refluxed for 3 hr. The water was then removed under aspirator pressure (30 mm.). The residue was dissolved in ethanol, added to an excess of picric acid dissolved in water, and allowed to stand overnight. The precipitate was removed and purified by crystallization from ethanol. Pertinent data about the picrates formed are given in Table II. Two of the picrates formed were converted to nitrate salts:

(a) 2-Imino-1,3-diazacyclopentane nitrate salt. This compound melted at 112.5–114.0°.

Anal. Calcd. for $C_3H_8N_4O_3$: C, 24.32; H, 5.44; N, 37.83. Found: C, 24.24; H, 5.40; N, 37.57.

(b) 2-Imino-1,3-diazacyclohexane nitrate salt. This compound melted at 160–161°.

Anal. Calcd. for $C_4H_{10}N_4O_3$: C, 29.63; H, 6.22; N, 34.55; Found: C, 29.54; H, 6.38; N, 34.29.

Nitration of 1-amino-3-guanidinopropane. 1-Amino-3-guanidinopropane dihydrochloride (2.0 g.) was added with cooling to 7 ml. of concentrated sulfuric acid. After all the salt had dissolved and the evolution of hydrogen chloride was complete, the solution was cooled to −30° and 4 ml. of 99% nitric acid was added. The nitration mixture was allowed to reach room temperature and held for 1 hr. The mixture was then poured over crushed ice and treated with a barium hydroxide solution until just acid to congo red paper. The barium sulfate was removed and the filtrate evaporated in a current of air. Barium nitrate crystallized and was removed as the solution was concentrated. The final residue weighed 2.08 g. (87%) and melted at 130–138°. After recrystallization from an ethanol-water solution, the salt melted at 140–141°. Considering the conditions used for nitration, this compound was probably the nitrate salt of 1-amino-3-nitroguanidinopropane. The ultraviolet absorption spectrum showed a maximum at 269–270 mμ which corresponded to a maximum obtained by McKay and Sandorfy[5] for the nitroguanidino group.

Anal. Calcd. for $C_4H_{12}N_6O_5$: C, 21.43; H, 5.39; N, 37.49. Found: C, 21.83; H, 5.62; N, 37.08.

The *nitrate* salt was converted to the picrate which melted at 190–192°.

Anal. Calcd. for $C_{10}H_{14}N_8O_9$: C, 30.77; H, 3.61; N, 28.71. Found: C, 30.99; H, 3.38; N, 28.90.

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[5] A. F. McKay and C. Sandorfy, *Can. J. Chem.*, **31**, 42 (1952).

Inhibition of the Nitrostyrene Condensation in Acetic Acid by Traces of Water[1]

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Catalysis by a primary amine in glacial acetic acid is frequently prescribed for the synthesis of β-nitrostyrenes from aromatic aldehydes and nitromethane.[2] In extending our earlier studies of

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[1] This work was supported by the Office of Ordnance Research, U. S. Army, and by the National Science Foundation. The kinetic studies are from the M.S. thesis of Charles E. Bell, Jr., University of Virginia, 1955.

[2] W. S. Emerson, *Chem. Revs.*, **45**, 347 (1949).

nitrostyrene formation[3,4] to these conditions, we noticed a striking effect of water, in low concentrations, upon the rate. A mechanistic interpretation of these observations is given in this paper.

The reaction of piperonal with nitromethane at 100.4° follows a second-order course at a given *n*-butylamine concentration. The rate constant, k_2, is proportional to the *n*-butylamine concentration, indicating third-order (pseudo second-order) kinetics. Figure 1 shows the dependence of k_2 on the water concentration.

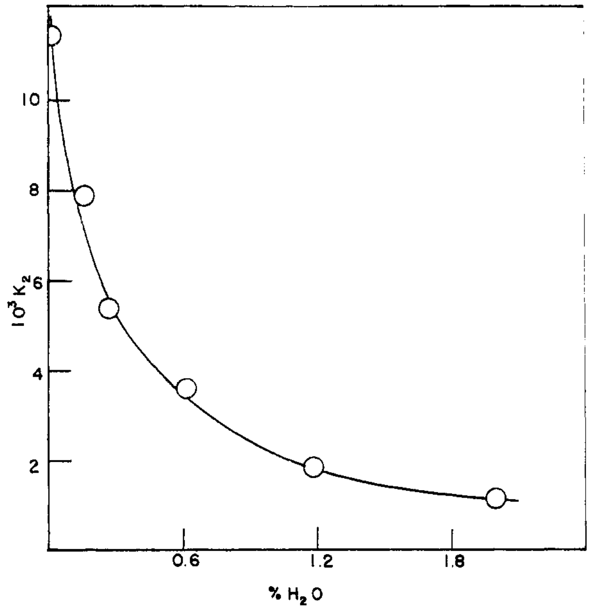

Fig. 1. Rate of nitrostyrene formation as a function of weight percent water in the solvent

Kolthoff and Bruckenstein[5] have made a careful study of the species present in acetic acid solutions of water and other bases. Before attempting a thorough kinetic investigation of acid-base catalysis of the reaction in so complex a mixture, we have simply correlated the observed effect of water with a reversal of the first step of the mechanism previously proposed, involving piperonylidene *n*-butylamine as intermediate.[4]

$$\mathrm{ArCHO + BuNH_2 \rightleftharpoons ArCH{=}NBu + H_2O} \qquad (1)$$

$$\mathrm{ArCH{=}NBu + CH_3NO_2 \rightarrow ArCH{=}CHNO_2 + BuNH_2} \qquad (2)$$

The concentration of this Schiff base is easily measured spectrophotometrically, in the absence of nitrostyrene, and the equilibrium constant for equation 1 calculated. The expression $K = (\mathrm{ArCH{=}NBu})(\mathrm{H_2O})/(\mathrm{ArCHO})(\mathrm{BuNH_2})$ apparently holds for stoichiometric concentrations, even though *n*-butylamine, water and the Schiff base must exist predominantly as their conjugate acids in acetic acid. The value of K at 100.4° is 0.18, the mean of sixteen measurements over a fifteen- to fifty-fold range in concentration of each of the reactants. Although the results are not very precise (the average deviation from the mean is 0.06) they serve to establish the fact that in the range of concentrations encountered in the kinetic studies, the extent of reaction of aldehyde with amine, to form Schiff base, cannot be neglected, and is given by the constant K.

At 25°, $K = 0.37$, which is smaller than in methanol[6] by a factor of nearly 10^4, possibly because the more complete ionization of *n*-butylamine, the strongest base present, shifts the equilibrium 1 to the left in acetic acid. In methanol, none of the species is appreciably ionized.

The initial concentration of Schiff base in any reaction mixture can now be calculated from K and the initial concentrations of *n*-butylamine, piperonal,[7] and water, for step 1 is comparatively

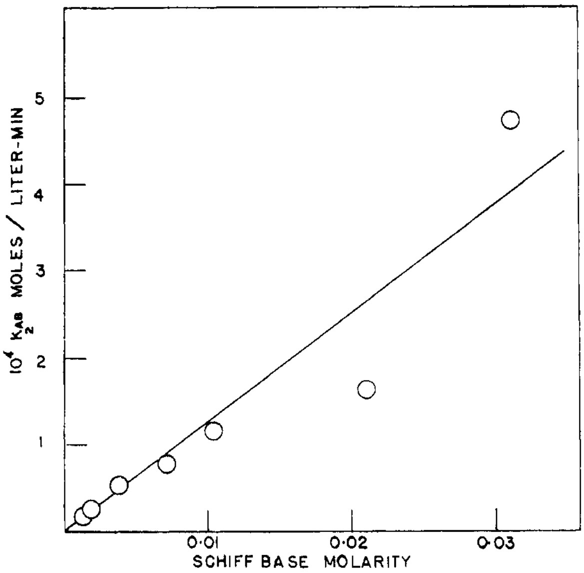

Fig. 2. Rate of nitrostyrene formation as a function of calculated Schiff base concentration

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[4] T. I. Crowell and D. W. Peck, *J. Am. Chem. Soc.*, **75**, 1075 (1953).

[5] I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1, 10 (1956).

[6] R. L. Hill, and T. I. Crowell, *J. Am. Chem. Soc.*, **78**, 2284, 6425 (1956).

[7] In one experiment, Schiff base was substituted for piperonal. The deviation of the point at 0.021*M* Schiff base in Fig. 2 could result from an increment of 0.02% in the water content of the solvent, which corresponds to the amount of water later found to be introduced with the *n*-butylamine. The lower points, obtained with the same sample of *n*-butylamine, are less sensitive to extraneous traces of water.

However, the water content of the *n*-butylamine used in the experiment starting with Schiff base (the point at 0.031*M*) was known and in this case incorporated into the calculation.

rapid and step 2 rate-controlling. Figure 2 shows the initial rate, k_2ab, plotted against this calculated Schiff base concentration. The straight line obtained indicates second-order kinetics involving the Schiff base and nitromethane concentrations, consistent with a mechanism in which the Schiff base or its conjugate acid is an intermediate.

As we stated earlier,[3] the existence of a Schiff base intermediate does not preclude catalysis by secondary and tertiary amines. Preliminary experiments led to the isolation of nitrostyrene when piperidine and triethylamine were substituted for *n*-butylamine. A 74% yield was obtained with *N*-butylacetamide, in analogy with the efficiency of acetamide as catalyst for condensations in acetic acid.[8] It is quite possible that piperonylidene *n*-butylamine was formed under these conditions.[9]

EXPERIMENTAL

Materials. Glacial acetic acid, reagent grade, was dried by adding either acetic anhydride or benzene and fractionating. The water content was found by Karl Fisher titration to be 0.03%. Other reagents were as previously described.[4]

Formation of piperonylidene *n*-butylamine in acetic acid was demonstrated by its preparation in 74% yield.

Kinetic studies. Piperonal (about 0.2 g.) was weighed into a volumetric flask and dissolved in acetic acid. Nitromethane, *n*-butylamine, and water were added with calibrated pipets before dilution to 50 ml. This solution was then divided into 5-ml. samples which were sealed in 12 mm. diameter Pyrex ampoules and immersed for the desired time in a polyethylene glycol bath at 100.4 ± 0.3°. The ampoules were removed at intervals, cooled, and opened, and the contents transferred quantitatively into a solution of 2,4-dinitrophenylhydrazine for gravimetric determination of the aldehyde.[3]

Equilibrium studies. A solution of *n*-butylamine, water, and piperonylidene *n*-butylamine or piperonal was prepared in a drybox and placed in the thermostat. Equilibrium was reached within a minute or two. A sample was withdrawn after 30 min. and pipetted into methanolic hydrochloric acid for spectrophotometric determination of the Schiff base conjugate acid.[4] The rather small temperature coefficient of K probably rendered any shift of equilibrium, due to cooling of the sample during transfer, unimportant in this work. Since this sample was the only volume measured at 100°, the resulting Schiff base concentration was multiplied by 1.08, the ratio d_{25}/d_{100} for acetic acid. Thus, the concentrations given in this paper refer to solutions at 25°. While K would be independent of concentration units, the rate constant, k_2, must be multiplied by 1.08 for conversion to l/mole min. at the reaction temperature.

The spectrum of the methanol dilution of the reaction mixture showed only the peaks of piperonal and Schiff base in concentrations equal in sum to the stoichiometric piperonal concentration.

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(8) A. C. Cope, *J. Am. Chem. Soc.*, **59**, 2327 (1937).

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New Synthesis of Dimethylaminodimethylborane

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In the course of preparing dimethylaminomethylchloroborane, $(CH_3)_2NB(CH_3)Cl$,[2] moderate amounts of dimethylaminodimethylborane, $(CH_3)_2NB(CH_3)_2$, were required. Previous syntheses of the latter compound[3–5] were conducted in vacuum trains, under conditions not easily attained in ordinary laboratory equipment.

We have found that $(CH_3)_2NB(CH_3)_2$ may be prepared in high yield and in reasonable quantity by the action of methyl Grignard reagent on dimethylaminodichloroborane, $(CH_3)_2NBCl_2$. This is the first direct application of a Grignard reagent to the synthesis of an aminodialkylborane. Similar applications to the synthesis of *B*-alkylborazines (*i.e.*, *B*-alkylborazoles) have recently been discussed.[6–8]

We believe that this reaction represents a general method for the synthesis of dialkyl (and, presumably, diaryl) boron compounds that have been prepared up to now only by more indirect or cumbersome methods. The dimethylamino group may be regarded as a blocking group and can subsequently be replaced if desired. For example, hydrolysis yields a dialkylhydroxyborane (i.e., borinic acid).

EXPERIMENTAL

The reaction is carried out in a three-neck flask, fitted with a dropping funnel and stirrer, and protected with a dry nitrogen atmosphere. Dimethylaminodichloroborane, diluted with 10 to 20 volumes of ether, is placed in the flask, which is then immersed in an ice bath. The theoretical amount of methyl Grignard reagent in ether is added dropwise over a 3-hr. period, after which the bath is removed. The stirring is continued until the solution and suspended magnesium salts have warmed to room temperature. The ether and the product are then distilled from the flask at reduced pressure, trapping them in a reservoir at Dry Ice temperature. The residual magnesium salts are heated briefly to insure complete separation of product. Subsequent fractional distillation of the ether solution yields a small forerun and a main fraction of $(CH_3)_2NB(CH_3)_2$, boiling at 63–65° at atmospheric pressure. The product of an early run was found to contain 16.2%N (theory, 16.5%) by a Kjeldahl procedure. The chlorine content was nil. Methanol gave an adduct, melting at 49–51° (lit. 51–53°).[4]

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