1002 *Inorg. Chem.* **1995,** *34,* 1002−1003

# Convenient Procedures for the Laboratory Preparation of Borazine

**Thomas Wideman and Larry G. Sneddon***

Department of Chemistry, University of Pennsylvania,
Philadelphia, Pennsylvania 19104-6323

*Received September 30, 1994*

## Introduction

The recent design and synthesis of a range of new inorganic polymers based on borazine, $B_3N_3H_6$,[1] has sparked new interest in the chemistry and properties of this ring compound. Borazine was originally discovered by Stock[2] in 1926; however, chemical studies, as well as practical applications of borazine, continue to be held back by the absence of efficient, economical synthetic routes. We report here simple, quick, one-step procedures by which multigram quantities of borazine may be produced from inexpensive starting materials using standard laboratory equipment.

## Experimental Section

All synthetic manipulations were carried out using standard vacuum or inert atmosphere techniques as described by Shriver.[3]

**Materials.** Sodium borohydride and ammonium sulfate were purchased from Aldrich and used as received. Tetraglyme was vacuum distilled from molten sodium shortly before use. Ammonia−borane was purchased from Callery Chemical Co. and used as received.

**Preparation of Borazine from Sodium Borohydride and Ammonium Sulfate.** In a typical reaction, a mixture of 30.7 g (0.81 mol) of $NaBH_4$ and 82.3 g (0.62 mol) of $(NH_4)_2SO_4$ were mixed with 350 mL of tetraglyme in a 2 L, three-neck round-bottomed flask which was fitted with a thermometer and reflux condenser. The exit of the reflux condenser was connected to a standard vacuum line[4] equipped with four liquid-nitrogen traps. The reaction mixture was gradually warmed to 135 °C over the course of 1 h and held at this temperature for an additional hour under a dynamic vacuum that was maintained at 2−5 Torr by the continuous removal of the evolved hydrogen and borazine through the vacuum line. Following the reaction, the borazine that had been retained in the liquid-nitrogen traps was further purified by a single vacuum fractionation through a −45, −78, and −196 °C trap-series to give (−78 °C trap) 13.1 g (0.16 mol, 59.9% based on starting $BH_4^-$) of borazine. No other products were detected in the IR, $^{11}B$ and $^1H$ NMR,[5] or GC/MS spectra of the product, and its vapor pressure (85 Torr at 0 °C) matched the literature value,[6] indicating that the borazine was obtained in excellent purity.

Following the completion of the reaction, analysis of the reaction mixture by $^{11}B$ NMR showed no discrete boron-containing species remained in the tetraglyme. In other experiments, these reaction mixtures were used again for a second preparation and were found to give slightly *increased* yields.

In an alternate procedure, similar to that described below for the pyrolysis of ammonia−borane, an intimate mixture of 21.8 g (0.58 mol) of $NaBH_4$ and 56.2 g (0.43 mol) of $(NH_4)_2SO_4$ was dropped into 350 mL of tetraglyme at 135 °C over 1 h and then allowed to react at that temperature for an additional 2 h. Fractionation of the material retained in the liquid-nitrogen traps gave 8.3 g (0.10 mol, 53.8%) of borazine.

**Preparation of Borazine from Ammonia−Borane.** In a typical reaction, a 2 L vacuum solid-addition funnel (Chemglass part no. CG-1723-99) containing 27.4 g (0.89 mol) of ammonia−borane was connected under a nitrogen flow to a 2 L, three-neck round-bottomed flask, which was fitted with a thermometer and reflux condenser, containing 750 mL of tetraglyme. The exit of the reflux condenser was connected to a standard vacuum line[4] equipped with four liquid-nitrogen traps. The tetraglyme was maintained at 140−160 °C and the ammonia−borane was slowly added over 3 h under a dynamic vacuum that was kept at 2−5 Torr by the continuous removal of the evolved hydrogen and borazine through the vacuum line. Following the reaction, the borazine that had been retained in the liquid-nitrogen traps was further purified by a single vacuum fractionation through a −45, −78, and −196 °C trap-series to give (−78 °C trap) 16.0 g (0.20 mol, 67.0% yield) of product. Spectral analysis and vapor pressure measurements again demonstrated that borazine was obtained in excellent purity.

## Results and Discussion

Borazine was first prepared by Stock[2] by the thermal decomposition of the diammoniate of diborane. Borazine has also been observed as a product in several other reactions,[7] but none of these are convenient for laboratory preparations. One of the best previous laboratory syntheses of borazine has involved the preparation of *B*-trichloroborazine[8] (eq 1) and its subsequent reduction by metal borohydrides[9] (eq 2).

$$3BCl_3 + 3NH_3 \rightarrow 2,4,6\text{-}Cl_3B_3N_3H_3 + 6HCl \qquad (1)$$

$$2,4,6\text{-}Cl_3B_3N_3H_3 + 3NaBH_4 \rightarrow H_3B_3N_3H_3 + 3NaCl + {}^3/_2B_2H_6 \qquad (2)$$

Even with the recent excellent improvements reported by Zakharkin,[10] this approach has a number of limitations including relatively small scales, long reaction times, difficult purification, the use of potentially carcinogenic solvents (i.e. chlorobenzene) and requires the handling of air-sensitive materials, including *B*-trichloroborazine and the diborane that is generated during the reduction step.

Two larger scale methods for the preparation of borazine have been achieved, but these methods employ equipment or procedures not generally feasible in the laboratory. The best commercial procedure is described in a patent issued to the Callery Chemical Co. Division of Mine Safety Appliances Co.[11]

---

(1) See, for example: Paine, R.; Sneddon, L. G. *CHEMTECH* **1994**, 29−37 and references therein.

(2) Stock, A.; Pohland, E. *Chem. Ber.* **1926**, *59B*, 2215−2223.

(3) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(4) See, for example, ref 3, p 101. We have also used a line similar to that in ref 3, p 102, with removable traps as seen on p 125.

(5) Gaines, D. F.; Borlin, J. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975; Chapter 7 and references therein.

(6) Stock, A. In *Hydrides of Boron and Silicon*; Cornell University Press: Ithaca, NY, 1933; p 94.

(7) (a) Stock, A.; Pohland, E. *Chem. Ber.* **1929**, *62B*, 90−99. (b) Stock, A.; Wiberg, E.; Martini, H. *Chem. Ber.* **1930**, *63B*, 2927−2937. (c) Stock, A.; Wiberg, E.; Martini, H.; Nicklas, A. *Chem. Ber.* **1932**, *65B*, 1711−1724. (d) Schlesinger, H. I.; Horvitz, L.; Burg, A. B. *J. Am. Chem. Soc.* **1936**, *58*, 409−414. (e) Schlesinger, H. I.; Ritter, D. M.; Burg, A. B. *J. Am. Chem. Soc.* **1938**, *60*, 1296−1300. (f) Schlesinger, H. I.; Ritter, D. M.; Burg, A. B. *J. Am. Chem. Soc.* **1938**, *60*, 2297−2300. (g) Wiberg, E.; Bolz, A. *Chem. Ber.* **1940**, *73B*, 209−232. (h) Wiberg, E. *Naturwissenschaften* **1948**, *35*, 182−188. (i) Videla, G. J.; Bühler, M. F. *Proc. Int. Conf. on Peaceful Uses of Atomic Energy* **1955**, *8*, 619. (j) Emeléus, H. J.; Videla, G. J. *J. Chem. Soc.* **1959**, 1306−1307. (k) Burg, A. B. *Inorg. Chem.* **1973**, *12*, 1448−1450.

(8) Brown, C. A.; Laubengayer, A. W. *J. Am. Chem. Soc.* **1955**, *77*, 3699−3700.

(9) (a) Schaeffer, R.; Steindler, M.; Hohnstedt, L.; Smith, H. S., Jr.; Eddy, L. B.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1954**, *76*, 3303−3306. (b) Hohnstedt, L. F.; Haworth, D. T. *J. Am. Chem. Soc.* **1960**, *82*, 89−92. (c) Dahl, G. H.; Schaeffer, R. *J. Inorg. Nucl. Chem.* **1960**, *12*, 380−381. (d) Niedenzu, K.; Dawson, J. W. *Inorg. Synth.* **1967**, *10*, 142−144.

(10) Zakharkin, L. I.; Ol'shevskaya, V. A. *Metallorg. Khim.* **1993**, *6*, 381−2.

(11) Hough, W. V.; Guibert, C. R.; Hefferan, G. T. U.S. Patent No. 4,150,097, April 17, 1979.

0020-1669/95/1334-1002$09.00/0

In this process, the batch pyrolysis of ammonia−borane dissolved in diglyme was found to produce borazine in 69−71% yields on 0.5−3 g scales. A more elaborate continuous flow process, involving a heated vertical steel reactor, was then used to make larger quantities of borazine, but the complicated design would be difficult to engineer in the laboratory.

The second procedure is based on the original discovery by Schlesinger[12] that the high temperature (300 °C) solid-state reaction of lithium borohydride and ammonium chloride yields borazine. Mikheeva and Markina[13] optimized these reactions and found that yields of 38−41% were obtained with a 2:1 excess of ammonium chloride, but the reaction required constant agitation by an unusual "motorless shaker". Similarly, Volkov[14] optimized the sodium borohydride and ammonium chloride reaction at 230 °C to produce borazine in yields of 13−23%, but again, an unusual apparatus consisting of a steel reactor and shaker and a metallic nickel trap was required. These solid-state reactions employ inexpensive starting materials, but have the disadvantages of complicated apparatus, variable and low yields, and the formation of side products, such as chloroborazine and diborane, which complicate purification and handling.

As described below, we reinvestigated the production of borazine from both ammonia−borane and from the borohydride−ammonium salt reaction with the aim of developing procedures that were both efficient and reliable and could be readily accomplished with normal laboratory equipment.

With small modifications, the basic Callery batch procedure can be adapted for laboratory scale preparations, and we have used the procedure described in the Experimental Section to prepare 10−20 g of borazine over 3−4 h in 65−70% yields.

$$3H_3N{\cdot}BH_3 \xrightarrow[\text{tetraglyme}]{140-160\ ^\circ\text{C, 3 h}} B_3N_3H_6 + 6H_2 \qquad (3)$$

In contrast to the procedure described by Callery, we have found that the slow addition of *solid* ammonia−borane, rather than an ammonia−borane solution, allows the reaction to be run continuously, since there is no increase in solvent volume. While commercially available, the expense of ammonia−borane is a limitation to this route. Alternatively, ammonia−borane can be made through several procedures,[15] but this adds an extra step to the borazine preparation.

In order to develop a more economical, one-step procedure, we reinvestigated the borohydride−ammonium salt reactions to prepare borazine. As discussed above, solid-state $NH_4Cl$/$NaBH_4$ (or $LiBH_4$) reactions have been used to produce borazine, but due to the complicated apparatus needed to maintain efficient mixing of the solids, these procedures have limited utility as a routine laboratory method. Alternatively, if these reactions could be carried out in solution, then such specialized equipment might not be necessary. Haworth[16] has reported that the reaction of sodium borohydride and ammonium chloride in ethereal solvents at 190−230 °C gives borazine in 35% yields. When we repeated this reaction in tetraglyme solution, however, we found significant amounts of chloroborazine (presumably from the reaction of borazine with hydrogen chloride), ammonia, and acetylene (resulting from tetraglyme reduction), necessitating careful, repeated fractionations of the products to give variable yields of 3−40%. As was proposed for the solid-state reactions,[12−14] the observed side products suggest at least partial decomposition of $NH_4Cl$ to $NH_3$ and HCl, which can then react with borazine in solution or during the subsequent fractionations.

In order to eliminate the production of the chlorinated products observed in the reactions with $NH_4Cl$, we investigated the use of other ammonium salts, including $(NH_4)_2SO_4$, $(NH_4)HSO_4$ and $(NH_4)_2HPO_4$. All of these salts produced borazine upon reaction with $NaBH_4$, but the best results were obtained in reactions using finely powdered $(NH_4)_2SO_4$ in a 0.65/1 $BH_4^-$/$NH_4^+$ molar ratio. Using the procedure described in the Experimental Section, in which the borazine is removed continuously in vacuo as it is formed, borazine may be produced in 10−20 g scales, in 58−60% yields, over 3 h, by the reaction of $NaBH_4$ and $(NH_4)_2SO_4$ in tetraglyme solution at 120−140 °C. Shore[15a] has previously shown that ammonia−borane is readily generated upon reaction of $LiBH_4$ with $(NH_4)_2SO_4$ in ether at room temperature. Thus, the reaction (eq 4) most likely involves the initial generation of ammonia−borane, followed by its pyrolysis to borazine (as in eq 3).[17]

$$3(NH_4)_2SO_4 + 6NaBH_4 \xrightarrow[\text{tetraglyme}]{120-140\ ^\circ\text{C, 3 h}} 2B_3N_3H_6 + 3Na_2SO_4 + 18H_2 \qquad (4)$$

The fact that the reactions of $NaBH_4$ with $(NH_4)_2SO_4$ proceed at lower temperatures (120−140 °C) than those with $NH_4Cl$ (190−230 °C) also appears to eliminate any solvent reduction byproducts. Indeed, since borazine is the only volatile product observed in the reaction, the compound is obtained in excellent purity even without vacuum fractionation. Thus, the $(NH_4)_2SO_4$/solution procedure is clearly favored over the previous solid-state syntheses, since only normal laboratory equipment is required, the product is obtained in excellent purity without extensive fractionations, and significantly higher yields are obtained. Likewise, the $(NH_4)_2SO_4$/solution procedure is also an improvement over the ammonia−borane route owing to the fact that the starting materials [$(NH_4)_2SO_4$ and $NaBH_4$] are inexpensive relative to ammonia−borane, yet the two procedures give comparable yields, purities and reaction times.

In conclusion, two excellent laboratory routes to the synthesis of borazine are now available. Preparations using either ammonia−borane or sodium borohydride−ammonium sulfate can both be run either by the continuous addition of the solids to a hot tetraglyme solution (facilitating larger scale preparations) or by the gradual warming of the solids in tetraglyme. The reaction of $(NH_4)_2SO_4$ and $NaBH_4$ is particularly attractive due to the inexpensive starting materials and now enables the convenient, *economical* generation of borazine.

**Acknowledgment.** We thank the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, for their support of this research. We also thank Dr. Joe Barendt at Callery Chemical Co. (Mine Safety Appliances Co.) for helpful discussions and Steve Yonemura and Steve Ware at Chemglass, Inc. for help in designing the vacuum solid-addition funnel.

IC941133M

---

(12) Schaeffer, G. W.; Schaeffer, R.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1951**, *73*, 1612−1614.

(13) Mikheeva, V. I.; Markina, V. Y. *J. Inorg. Chem., USSR* **1956**, 56−63. See also: Mikheeva, V. I.; Markina, V. Y. *Zhur. Neorg. Khim.* **1956**, *1*, 2700−2707.

(14) (a) Volkov, V. V.; Bagryantsev, G. I.; Myakishev, K. G. *Russ. J. Inorg. Chem.* **1970**, *15*, 1510−1513. (b) Volkov, V. V.; Pukhov, A. A.; Myakishev, K. G. *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk.* **1983**, *3*, 116−123.

(15) (a) Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 6084−6085. (b) Shore, S. G.; Böddeker, K. W. *Inorg. Chem.* **1964**, *3*, 914−915. (c) Hu, M. G.; Van Paasschen, J. M.; Geanangel, R. A. *Inorg. Nucl. Chem.* **1977**, *39*, 2147−2150.

(16) Haworth, D. T.; Hohnstedt, L. F. *Chem. Ind. (London)* **1960**, 559−560.

(17) (a) Hu, M. G.; Geanangel, R. A.; Wendlandt, W. W. *Thermochim. Acta.* **1978**, *23*, 249−255. (b) Wang, J. S.; Geanangel, R. A. *Inorg. Chim. Acta.* **1988**, *148*, 185−190.