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Reactions of Borazines in Liquid Ammonia

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The chemistry of the borazines has been primarily concerned with developing methods of synthesis and studying the types of reactions which these compounds undergo.[1] In general, symmetrically substituted borazines are relatively easy to prepare in comparison with the unsymmetrical derivatives. The borazine ring undergoes both addition and substitution reactions; substitution occurs more readily at the boron positions than at the nitrogen sites.[1]

As part of a general investigation of the formation and characterization of metal derivatives of the borazines, we became interested in the possibility of preparing reactive alkali metal derivatives of these compounds which might be used as synthetic intermediates. It is well known that the N-hydrogen atoms in primary and secondary amines are acidic, and metallic derivatives of these compounds can be formed by reaction with active metals or strong bases. Accordingly, the N-hydrogen atoms in borazines might be expected to show some acidic properties, a suggestion which is at least partially supported by the formation of N-lithiopentamethylborazine in the reaction of pentamethylborazine with methyllithium (eq 1).[2] The use of liquid ammonia as a reaction medium was suggested by numerous observations that very basic species, such as the solvated electron and the amide ion, are stable in this solvent and that the basic character of this solvent tends to enhance the apparent acidity of weakly acidic substances.[3]

$$HN_3(CH_3)_2B_3(CH_3)_3 + CH_3Li \longrightarrow LiN(CH_3)_2B_3(CH_3)_3 + CH_4 \quad (1)$$

Experimental Section

Reactions in liquid ammonia were conducted in vessels which contained a sintered-glass frit permitting isolation of solid products from the solvent.[4] The vessels could be arranged in series to provide a versatile sequence of filters and/or reactors that could be evacuated with a mechanical-backed oil diffusion pump or filled with either gaseous ammonia or dry nitrogen. Solid reactants could be introduced into the reaction vessels in a drybox, by using a weighing pistol, or could be added to the system against a brisk stream of dry nitrogen or ammonia; liquids were introduced with a syringe. Filtration was achieved by creating a pressure differential between the container carrying the solution and the vessel into which the solution was to be filtered.

Anhydrous ammonia was prepared by distilling the commercial product from sodium. Ammonia solutions of the alkali metal amides were prepared by allowing the blue alkali metal–ammonia solutions to decompose in the presence of catalytic amounts of metallic iron; the alkali metal amide solutions were filtered prior to use.

A mixture of B-trimethyl-, N-methyl-B-trimethyl-, N-dimethyl-B-trimethyl-, and hexamethylborazine was prepared by the copyrolysis of $(CH_3)_3BNH_3$ and $(CH_3)_3BNH_2CH_3$ and was separated by conventional methods.[2] B-Triphenyl-,[5] N-trimethyl-,[6] N-triphenyl-,[7] and hexaphenylborazine[8] were prepared and purified by methods described in the literature.

Analyses were carried out by digesting the borazine-containing compound in a mixture of concentrated H_2SO_4 and 30% H_2O_2 and determining boron titrimetrically[9] and nitrogen by the conventional Kjeldahl procedure. The alkali metals were determined with a Beckman flame photometer using standard procedures; potassium was weighed as $KB(C_6H_5)_4$.[10] Carbon and hydrogen were determined by standard combustion techniques.

Reaction of Borazines with Alkali Metals.—The general procedure involved the use of three reaction vessels in series. An alkali metal–ammonia solution was prepared in the first vessel. The second vessel contained the borazine and liquid ammonia, and the third vessel was used to receive the filtrate from the reaction mixture. By adjusting the pressure in the system, the metal–ammonia solution was forced through a frit into the second vessel which contained the borazine; the reaction mixture was then filtered into the third vessel. Solid products which separated in the course of the reaction were retained in the reaction vessel by the frit and were washed with liquid ammonia before being worked up in the conventional manner. Evaporation of the solvent from the filtrate contained in the third vessel yielded the ammonia-soluble products.

(a) **Reaction of $(C_6H_5)_3B_3N_3H_3$ with Alkali Metals.**—B-Triphenylborazine is essentially insoluble in liquid ammonia at its boiling point (0.6 mg/ml); however, it reacts with alkali metal–ammonia solutions to form a red soluble product. In a typical experiment, 2.00 g (6.47 mmoles) of B-triphenylborazine suspended in 50 ml of anhydrous ammonia reacted with 0.26 g (6.5 mg-atoms) of potassium to yield a red solution, which upon filtration and evaporation of the solvent gave a red crystalline product. The product slowly lost its color during several hours of continuous evacuation, retaining only a slight coloration. The final product (1.55 g) melted at >230° in a sealed capillary, undergoing a series of vivid color changes as the temperature was increased.

Anal. Calcd for $(C_6H_5)_3B_3N_3H_3 \cdot KNH_2$: C, 59.40; H, 5.54; B, 8.91; K, 10.78; N, 15.40. Calcd for $(C_6H_5)_3B_3N_3H_3 \cdot K$: C, 62.10; H, 5.27; B, 9.32; K, 11.23; N, 12.07. Calcd for $(C_6H_5)_3B_3N_3H_2K$: C, 62.28; H, 5.00; B, 9.34; K, 11.27; N, 12.11. Found: C, 59.14; H, 5.50; B, 8.48; K, 11.25; N, 15.56.

Attempts to analyze the initial red product gave variable results; the nitrogen analysis was usually higher than that calculated for either the potassium or the potassium amide adduct.

Similar results were obtained in the reactions of sodium– or lithium–ammonia solutions with B-triphenylborazine. The analyses varied between those expected for an alkali metal adduct, $(C_6H_5)_3B_3N_3H_3 \cdot M$ [or the alkali metal salt of the borazine $(C_6H_5)_3B_3N_3M$], and the alkali metal amide adduct $[(C_6H_5)_3B_3N_3H_3 \cdot MNH_2]$, depending upon the time that elapsed between formation of the red liquid ammonia solution and isolation of the product. Attempts to carry out the reaction of the borazine with 3 moles of alkali metal led to degradation of the borazine ring.

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A solution of the red product in dry tetrahydrofuran at 23° exhibited a three-line esr signal 34–44 gauss wide which has thus far resisted resolution into finer components. The red liquid ammonia solution decolorized upon the addition of NH_4Cl giving a white precipitate which was identified as B-triphenylborazine by its infrared spectrum and melting point, 176–178°; lit.[5] 179–182°.

In another experiment, sodium (0.037 g, 1.64 mg-atoms) was allowed to react with B-triphenylborazine (0.5661 g, 1.83 mmoles) in boiling ammonia while anhydrous ammonia gas was passed through the system and the effluent gases collected over aqueous H_2SO_4; 19.9 ml (STP) (0.89 mmole) of a noncondensable gas, identified as hydrogen by its characteristic reaction with oxygen, was collected.

The products of the reaction between B-triphenylborazine and potassium reacted with water to give B-triphenylborazine and with methyl iodide to form methylamine, potassium iodide, and B-triphenylborazine.

N-Triphenylborazine is essentially insoluble in liquid ammonia and does not alter the characteristic blue color of metal–ammonia solutions. Qualitative observations on hexaphenylborazine, available in very limited amount, indicate that this borazine is insoluble in ammonia but dissolves in potassium–ammonia solutions to give a red solution.

(b) **Reaction of Methylborazines with Alkali Metals.**—The results of several experiments using the general technique described above indicate that B-trimethylborazine, which is miscible with ammonia, does not discharge the blue color associated with potassium–ammonia solutions at the boiling point of the solvent; unreacted borazine was recovered after evaporation of the solvent. Hexamethylborazine is insoluble in boiling liquid ammonia and does not dissolve in a potassium–ammonia solution after refluxing for several hours. Evaporation of the solvent yields the starting materials unchanged.

N-Trimethylborazine is soluble in ammonia but reacts with it to give a viscous liquid which decolorizes potassium–ammonia solutions with the liberation of hydrogen. These reactions were not investigated further because it was apparent that the borazine ring had been destroyed.

Reaction of $(C_6H_5)_3B_3N_3H_3$ with KNH_2.—Potassium (0.440 g, 11.2 mg-atoms) was dissolved in about 25 ml of ammonia, metallic iron was added, and the solution was allowed to boil until the characteristic blue color disappeared. The resultant pale green solution was then filtered into the second reaction vessel, which contained 3.24 g (10.5 mmoles) of B-triphenylborazine; most of the latter compound dissolved but no color change was observed in the process. This mixture was allowed to boil for several minutes and then filtered into a third flask; the unreacted B-triphenylborazine remained on the frit. Evaporation of the filtrate yielded a colorless powder (3.02 g) that did not melt below 230°. The infrared spectrum of the product was identical with that of the product formed from the reaction of potassium and B-triphenylborazine in ammonia.

Anal. Calcd for $(C_6H_5)_3B_3N_3H_3 \cdot KNH_2$: C, 59.40; H, 5.54; B, 8.91; K, 10.78; N, 15.40. Found: C, 59.61; H, 5.35; B, 8.75; K, 10.86; N, 15.53.

Results and Discussion

B-Alkyl- and -arylborazines appear to be reasonably stable in liquid ammonia for short periods of time; however, borazines possessing B–H bonds react with this solvent to form products corresponding to the fission of the borazine ring. The latter observation is in agreement with reports that the parent compound reacts slowly with liquid ammonia to form glassy residues of indefinite composition.[9] Alkyl-substituted compounds are generally more soluble than the corresponding aryl compounds. The anticipated acidity of the N-hydrogen atom in borazines did not materialize in liquid ammonia solutions with the strongest bases possible in that medium, *i.e.*, the solvated electron and NH_2^-, and with electron-withdrawing groups, *i.e.*, phenyl groups, at the boron sites.

The reaction of metal–ammonia solutions with B-phenylborazines yields a deep red solution containing a paramagnetic species (eq 2) which is slowly converted

$$(C_6H_5)_3B_3N_3H_3 + M \longrightarrow [(C_6H_5)_3B_3N_3H_3]\cdot{}^-M^+ \qquad (2)$$

into an alkali metal amide adduct with the liberation of hydrogen. The formation of radical anions by B-phenylborazines and the absence of reaction in the case of N-phenylborazines are consistent with the relative ease of reduction of phenylborazines at a dropping mercury electrode and the stability of the radical anion formed.[11] The potassium amide adduct of B-triphenylborazine was prepared by the direct reaction of these two substances (eq 3) and shown to be identical with

$$(C_6H_5)_3B_3N_3H_3 + KNH_2 \longrightarrow (C_6H_5)_3B_3N_3H_3\cdot KNH_2 \qquad (3)$$

the compound prepared from the reaction of the borazine and the alkali metal (eq 4). Attempts to discern

$$[(C_6H_5)_3B_3N_3H_3]\cdot{}^-M^+ + NH_3 \longrightarrow (C_6H_5)_3B_3N_3H_3\cdot MNH_2 + {}^1/_2H_2 \qquad (4)$$

the presence of significant amounts of the deprotonated borazine, which would be formed if the N-hydrogen atoms were acidic (eq 5), by isolating the product ex-

$$(C_6H_5)_3B_3N_3H_3 + M \longrightarrow (C_6H_5)_3B_3N_3H_2{}^-M^+ + {}^1/_2H_2 \qquad (5)$$

pected from its subsequent reaction with methyl iodide (eq 6) were unsuccessful. In all cases, the original B-

$$(C_6H_5)_3B_3N_3H_2{}^-M^+ + CH_3I \longrightarrow (C_6H_5)_3B_3N_3H_2CH_3 + MI \qquad (6)$$

triphenylborazine was obtained together with the products of the reaction between methyl iodide and the alkali metal amide. The adduct reacted with water (eq 7) and with ammonium ions (eq 8) in liquid am-

$$(C_6H_5)_3B_3N_3H_3\cdot KNH_2 + H_2O \longrightarrow (C_6H_5)_3B_3N_3H_3 + KOH + NH_3 \qquad (7)$$

$$(C_6H_5)_3B_3N_3H_3\cdot KNH_2 + NH_4^+ \longrightarrow (C_6H_5)_3B_3N_3H_3 + NH_3 + K^+ \qquad (8)$$

monia to liberate B-triphenylborazine as expected.

The alkali metal amide adducts described here represent the first reported case of the borazine being associated with a single adduct molecule. A 2:1 adduct between bromine and borazine has been reported;[9b,c] in all other instances 3:1 adducts are formed.[1] The BN framework of the borazine ring in the 3:1 adducts is isostructural with the carbon skeleton in the chair form of cyclohexane,[12] but the structure of the 2:1 adduct is unknown.

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