Boron Nitrogen Chemistry. II.[1] The Ring Cleavage of Borazine by Amines[2a]

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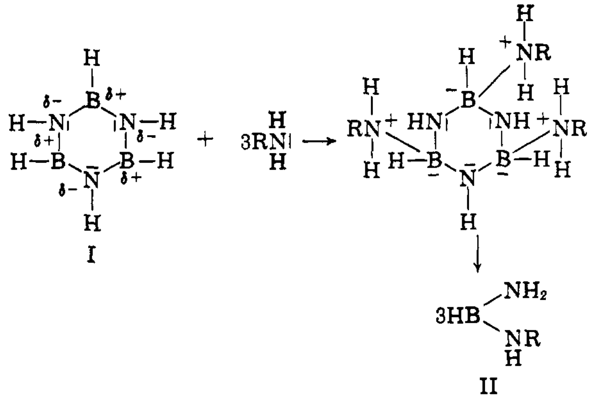
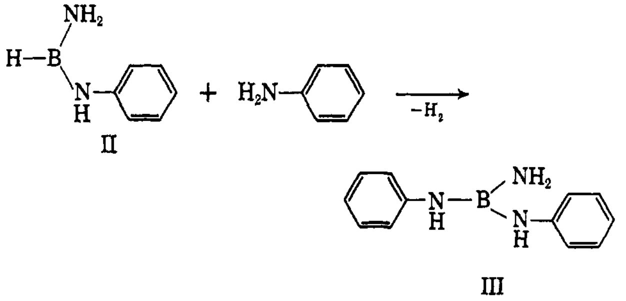
Because of the difference in electronegativities of the ring members in borazine (I), the boron atoms represent sites of attack by nucleophiles. Through the reaction with primary aromatic amines, borazine is cleaved and becomes at the same time an aminoborinylation agent. Thus, the reaction of I with aniline leads to N,N′-diphenyltriaminoborine (III). Structure proof of III has been adduced by methanolysis leading to trimethoxyborine–ammonia (V), the identity of which was established by synthesis.

Interest in the properties of compounds containing the boron–nitrogen combination in place of a —C═C— unit led us to investigate the formation of B–N bonds by intermolecular reactions. While the condensation of *o*-phenylenediamine with boronic acids yields stable cyclic systems,[3–5] the condensation of *p*-phenylenediamine with benzeneboronic acid could not be effected even in refluxing xylene with azeotropic removal of water. Negligible dehydration occurred, and the starting materials were recovered.

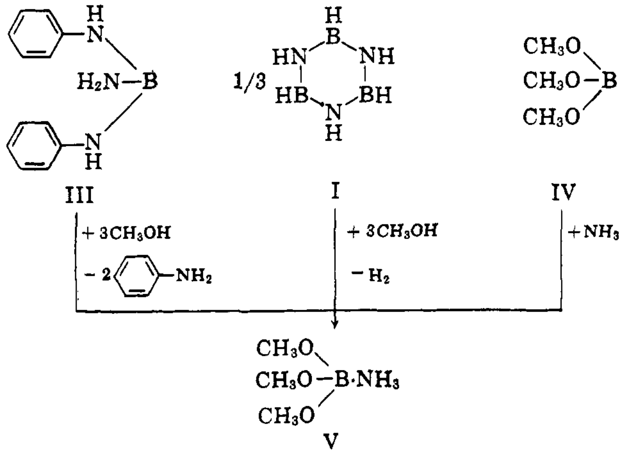
Since an intermolecular boron–nitrogen bond could not be formed by boronic acid condensation, the use of the preformed B–N unit in borazine for this purpose was examined. Borazine (I) resembles *s*-triazine in its planar aromatic structure,[6,7] and the greater difference in electronegativity in I should render it even more susceptible to nucleophilic attack than *s*-triazine. The latter undergoes cleavage with amines at room temperature to form three N,N′-disubstituted formamidine structures.[8] The corresponding reaction of borazine would be expected by analogy to give diaminoborines (II).



The reaction of borazine (I) with aniline was in fact found to be highly exothermic, and a diluent is required. Hydrogen was evolved, and a colorless crystalline solid was obtained. The infrared spectrum of this product contained a strong band for the B–N stretching mode[9] at 1500 and 1460 cm.$^{-1}$, but no band due to a B–H bond.[10] These data and the presence of 10 aromatic protons in the n.m.r. spectrum indicated that the product was the triaminoborine III. This product is evidently formed from the intermediate II by reaction with another mole of aniline and loss of hydrogen, and the over-all reaction is thus formally an aminoborinylation.



Further evidence for the structure of triaminoborine III was obtained by reaction with methanol to give a highly volatile white solid. The infrared spectrum of this product contained bands for B–N[9] at 1480 and 1460, NH_3^+[11,12] (1340 and 3150), and B–O[10] (1360 cm.$^{-1}$) which suggested that the compound was trimethoxyborine–ammonia (V),[13] first obtained in the reaction of borazine (I) and methanol,[14] and later



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[1] Part I: A. Kreutzberger and F. C. Ferris, *J. Org. Chem.*, **27**, 3496 (1962).

[2] (a) Presented at the 142nd National Meeting of the American Chemical Society in Atlantic City, N. J., Sept. 1962. (b) Institut für Pharmazie und Lebensmittelchemie der Universität Münster, Münster (Westfalen), Germany.

[3] D. Ulmschneider and J. Goubeau, *Ber.*, **90**, 2733 (1957).

[4] M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

[5] R. T. Hawkins, W. J. Lennarz, and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 3053 (1960).

[6] C. W. Rector, G. W. Schaeffer, and J. R. Platt, *J. Chem. Phys.*, **17**, 460 (1949).

[7] J. Goubeau, E. L. Jahn, A. Kreutzberger, and C. Grundmann, *J. Phys. Chem.*, **58**, 1078 (1954).

[8] A. Kreutzberger, *Fortschr. Chem. Forsch.*, **4**, 273 (1963).

[9] W. Gerrard, H. R. Hudson, E. F. Mooney, I. M. Stripp, and H. W. Willis, *Spectrochim. Acta*, **18**, 149 (1962).

[10] L. J. Bellamy, W. Gerrard, M. F. Lappert, and R. L. Williams, *J. Chem. Soc.*, 2412 (1958).

[11] I. R. Beattie and H. J. V. Tyrrell, *ibid.*, 2849 (1956).

[12] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *ibid.*, 2712 (1956).

[13] D. T. Haworth and L. F. Hohnstedt, *J. Am. Chem. Soc.*, **81**, 842 (1959).

[14] E. Wiberg and A. Bolz, *Ber.*, **73**, 209 (1940); E. Wiberg, *Naturwissenschaften*, **35**, 212 (1948).

synthesized directly from trimethyl borate (IV) and ammonia.[15]

The identity was established by direct comparison with a synthetic sample.

The reaction of borazine and *p*-nitroaniline proceeded in the same way as in the case of aniline to give hydrogen and N,N′-bis(*p*-nitrophenyl)triaminoborine.

It appears that this aminoborinylation of primary amines may be a general reaction. The reaction of borazine and ammonia leads to an unstable product which has not been characterized[14,16]; it is likely that a similar aminoborinylation occurs in this reaction also.

Experimental[17]

N,N′-Diphenyltriaminoborine (III).—Optimum conditions were obtained in runs carried out as follows. To a mixture containing 40.3 g. (0.5 mole) of borazine (I) in 150 ml. of dry benzene was added at room temperature and with agitation a total of 279.4 g. (3.0 moles) of aniline at such a rate that 50° was not exceeded. The reaction was accompanied by the evolution of hydrogen. After refluxing for 4 hr., the mixture was cooled to room temperature. The resulting crystals were vacuum-filtered under nitrogen and washed with pure anhydrous benzene; the yield was 220 g. (69.5%). Upon recrystallization from dry benzene, III was obtained as white stout prisms, m.p. 201–202°. The compound tends to decompose gradually upon storage for extended periods of time.

Anal. Calcd. for $C_{12}H_{14}BN_3$: B, 5.13; N, 19.91. Found: B, 5.39; N, 19.81.

N,N′-Bis(*p*-nitrophenyl)triaminoborine.—A suspension containing 41.4 g. (0.3 mole) of *p*-nitroaniline in 240 ml. of dry ether was added gradually to a mixture containing 8.0 g. (0.1 mole) of borazine (I) in 30 ml. of dry ether. An analysis of the gas evolved showed this to be hydrogen; no ammonia was detected. After boiling for 3 hr., ether was removed by distillation, 200 ml. of diglyme was added, and the reaction mixture was boiled again for 4 hr. The contents were allowed to come to room temperature and then filtered. The filtrate yielded N,N′-bis(*p*-nitrophenyl)triaminoborine as a slightly yellowish solid melting at 244–246°. The yield was 17.5 g. (38.7%).

Anal. Calcd. for $C_{12}H_{12}BN_5O_4$: B, 3.59; N, 23.26. Found: B, 3.78; N, 22.99.

Reaction of N,N′-Diphenyltriaminoborine (III) with Methanol.—Upon adding 6.3 g. (0.3 mole) of III to 15 g. of absolute methanol, an immediate reaction set in which was accompanied by a considerable amount of heat. When the vigorous reaction ceased, the contents were kept boiling for 1 hr., during which time the solid reaction product sublimed into the reflux condenser. The crystalline sublimate was recovered by scraping and was identified as trimethoxyborine–ammonia (V); weight 3.6 g. (100% yield). The product was purified by repeated sublimation and was obtained in the form of fine white needles melting at 75–76°. This melting point was not depressed when a sample of this substance was mixed with authentic samples obtained by methods described below.

Anal. Calcd. for $C_3H_{12}BNO_3$: B, 8.95; N, 11.58. Found: B, 8.83; N, 11.31.

Reaction of Borazine (I) with Methanol.—Inasmuch as there are no experimental details given in the original publication[14] mentioning this reaction for the first time, the reaction conditions used in this laboratory may be summarized as follows. To 4.0 g. (0.05 mole) of borazine (I) was added 30 g. of absolute methanol and the mixture was refluxed for 1.5 hr. During this heating period hydrogen gas was evolved and a white crystalline sublimate was trapped in the reflux condenser. The sublimate was identified as trimethoxyborine–ammonia (V) and was obtained in an amount of 14.8 g. (81.5% yield), m.p. 75–76°. Purification was accomplished by resublimation.

Anal. Calcd. for $C_3H_{12}BNO_3$: B, 8.95; N, 11.58. Found: B, 9.03; N, 11.29.

Trimethoxyborine–Ammonia (V) from Trimethyl Borate (IV).—Authentic trimethoxyborine–ammonia (V) was obtained from trimethyl borate and ammonia in anhydrous ether at −80° according to a described method.[15] The substance was obtained in a yield of 83.1%, purified by sublimation, and exhibited a melting point of 75–76°.

Anal. Calcd. for $C_3H_{12}BNO_3$: B, 8.95; N, 11.58. Found: B, 8.93; N, 11.50.

Infrared spectra were recorded with a Perkin-Elmer double-beam spectrophotometer, Model 237. Liquid substances were measured undiluted. To avoid disturbances by absorption bands caused by dispersion media, measurements on solid substances were made in the range of 4000–1350 cm.$^{-1}$ in "Fluorolube MO-10"[18] and in the range of 1350–625 cm.$^{-1}$ in Nujol.

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[15] J. Goubeau and U. Böhm, *Z. anorg. allgem. Chem.*, **266**, 161 (1951).

[16] A. Stock and E. Pohland, *Ber.*, **59**, 2215 (1926).

[17] Melting points are stated as determined with sealed capillary tubes.

[18] The trade-name "Fluorolube MO-10" has been assigned by the Hooker Chemical Corp., Niagara Falls, N. Y., to an oil being essentially a polymer of chlorotrifluoroethylene.

Synthesis of 1,4-Diolefins[1]

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The thermally initiated reaction of acetylene with olefins containing four to eight carbon atoms was studied in a flow system at 2500 p.s.i. and 350°. The 1:1 addition products obtained were nonconjugated, 1,4-diolefins. For example, butene-1, butene-2, and isobutylene produced 1,4-hexadiene, 3-methyl-1,4-pentadiene, and 2-methyl-1,4-pentadiene, respectively. A large excess of olefin in the reaction mixture was used to facilitate control of temperature and to improve the selectivity of the exothermic reaction. With 10 wt. % acetylene in the feed, the crude effluent from most reactions contained 3–9 wt. % 1,4-diolefins when 50% of the acetylene was converted. This corresponded to an efficiency of about 40% in conversion of both acetylene and olefin feed for the better reactions. The remainder formed heavier liquid products. Most of the diolefin products obtained are in accord with a mechanism involving a pseudo six-membered ring as an intermediate.

The thermally initiated reaction of acetylene with olefins has been studied over a period of many years. Early workers[2] reported the conjugated diolefins, butadiene and isoprene, as reaction products of ethylene and propylene with acetylene. However, the reactions were done at atmospheric pressure and temperatures up to 500°.

The reaction has now been investigated at higher pressures and lower temperatures. At 2500 p.s.i. and 350°, acetylene reacts with a number of olefins having four to eight carbon atoms to produce nonconjugated 1,4-diolefins as the only 1:1 adduct. Isomerization

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[1] Presented before the Division of Petroleum Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill.; Preprints, Vol. 9, No. 3, p. 187 (1964).

[2] Berthelot, *Ann. chim. phys.*, [6] **5**, 136 (1885); *Ann. chim.*, [4] **9**, 469 (1866).