533. H.R. Henne and P.E. Smith, J. Amer. Chem. Soc., 65, 1090 (1943).
534. W.B. Walley, E.L. Anderson, F. Duggan, J.W. Wilson, and G.E. Ullot, ibid., 77, 745 (1955).
535. J. Stanek and J. Sidlo, Ceskoslov. Farm., 2, 117 (1953); Chem. Abs., 49, 6123 (1955).
536. N.R. Boon and C.H. Vasey, U.S. Pat. 2660 056 (1954); Chem. Abs., 49, 9045 (1955).
537. C.H. Vasey, U.K. Pat. 734 511 (1955); Chem. Abs., 50, 7881 (1956).
538. L. Monti and G. Tranchi, Gazzetta, 81, 764 (1951).
539. L.I. Rapaport and Ya.A. Fialkov, Zhur. Obshch. Khim., 26, 279 (1956).
540. A. Einhorn, Annalen, 359, 145 (1908).
541. R. Bârre and A. Jaques, Rev. Can. biol., 1, 454 (1942); Chem. Abs. 36, 3853 (1942).
542. C. Lapière, Analyt. Chim. Acta, 1, 390 (1947).
543. J. Zwikker, Pharm. Weekblad, 68, 975 (1931).
544. J. Kubis and N. Liskova, Casopis Lekaru Cekých., 93, 602 (1954); Chem. Abs., 48, 11 724 (1954).
545. K.P. Agrilês and J.M. Beguiristain, Arch. med. exptl., 16, 145 (1953); Chem. Abs., 48, 5738 (1954).
546. G.G. Robles, Bol. Soc. quim. Peru, 15, 70 (1949); Chem. Abs., 44, 1648 (1950).
547. W. Bock, Chem. Ber., 55, 3400 (1922).
548. M. Pesez, J. Pharm. Chim., 28, 379 (1938); Chem. Abs., 33, 7961 (1939).
549. H. Rafalowska, Roczniki Panstwowego Zakladu Hig., 2, 226 (1951); Chem. Abs., 46, 4747 (1952).
550. E.B. Parkes, Analyst, 75, 448 (1950).
551. E. Emerson and L.C. Beegle, J. Org. Chem., 8, 425 (1943).
552. J. Deshusses, Pharm. Acta Helv., 20, 199 (1945); Chem. Abs., 42, 6055 (1948).
553. Han Chen Ho and Chu Ning Tao, J. Chinese Chem. Soc. (Formosa), 17, 79 (1950); Chem. Abs., 44, 5270 (1950).
554. B. Lilliman, Analyst, 75, 626 (1950).
555. A. Kofler, Mikrochem., 33, 4 (1947).
556. M. Brandstätter and H. Grimm, Mikrochim. Acta, 1175 (1956).
557. O. Schales, Chem. Ber., 71B, 116 (1938).
558. M. Brandstätter, Z. phys. Chem., 191A, 227 (1942).
559. Tso' Yuck Huang, Acta Pharm. Intern., 2, 43, 95 (1951); Chem. Abs., 46, 4172, 7284 (1952).
560. V. Hahn, Z. Kochansky, J. Gustak-Masek, and K. Jemric, Croat. Chem. Acta, 28, 119 (1958).
561. C. Stainier, J. Pharm. Belg., (N.S.), 5, 26 (1950); Chem. Abs., 44, 6575 (1950).
562. R. Fabre, Bull. Soc. chim. France, 33, 781 (1923).
563. R.S. McCutcheon and E.M. Plein, J. Amer. Pharmaceut. Assoc. (Sci. Edn.), 38, 24 (1949).
564. A. Lespanol and R. Delsarte, Ann. méd. légale criminol. police Sci., 16, 601 (1936); Chem. Abs., 31, 1954 (1937).
565. C. Stainier, C. Lapiere and S. de Tiège-Robinet, Ann. pharm. franc., 14, 384 (1956).
566. C. Raeth and R. Gebauer, U.S. Pat. 2 134 672 (1939); Chem. Abs., 33, 994 (1939).
567. P. Bouchereau, J. Pharm. Chim., 28, 484 (1938); Chem. Abs., 33, 8565 (1939).
568. P. Beiersdorf and Co., A.-G., German Pat. 659 221 (1938); Chem. Abs., 32, 5592 (1938); Chem. Abs., 32, 5592 (1938).
569. H. Ruhkopf, Chem. Ber., 70, 939 (1937).
570. C. Stainier, C. Lapiére, and S. de Tiége-Robinet, Ann. pharm. franc., 14, 476 (1956).
571. G.H. Wagenaar, Pharm. Weekblad, 78, 345 (1941); Chem. Abs., 38, 2454, (1944).
572. G. Beck, Mikrochem., 29, 206 (1941).
573. H. Kaiser and W. Lang, Pharm. Zentralhalle, 91, 281 (1952); Chem. Abs., 47, 675 (1953).
574. C.J. de Molf, Pharm. Weekblad, 84, 537 (1949); Chem. Abs., 44, 279 (1950).
575. W. Paulus and H.J. Mallach, Arzneimittel - Forsch., 4, 391 (1954); Chem. Abs., 48, 11 001 (1954).
576. A. Kyaer and K. Rubinstein, Acta Chem. Scand., 7, 528 (1953).
577. A. Calo, A. Mariani, and O. Mariani-Morelli, Rend. 1-st Super Sanita, 20, 811 (1957).
578. A.N. Kurteva, Zavod. Lab., 9, 307 (1940).
579. M. Schubert, Z. analyt. Chem., 107, 374 (1936).
580. P. Chavanne and H. Maric, Ann. pharm. franc., 11, 91 (1953); Chem. Abs., 47, 6605 (1953).
581. R. Heiz, Dansk. Tidsskr. Farm., 26, 69 (1952); Chem. Abs., 46, 6551 (1952).
582. S. Goldschmidt, W. Lamprecht, and E. Helmreich, Z. physiol. Chem., 292, 125 (1953).
583. A. Grieg, Nature, 170, 845 (1952).
584. L.K. Goldbaum, Analyt. Chem., 24, 1604 (1952).
585. C.J. Umberger and G. Adams, ibid., 24, 1309 (1952).
586. L. Levi and C.E. Hubley, ibid., 28, 1591 (1956).
587. A. Kalvoda and J. Zyka, Cesk. Farm., 2, 154 (1953); Chem. Abs., 48, 9672 (1954).
588. O. Manousek and P. Zuman, ibid., 5, 193 (1956); Chem. Abs., 50, 17 334 (1956).

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BORAZOLE AND ITS DERIVATIVES

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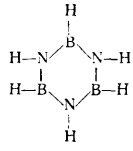
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INTRODUCTION

Borazole is a six-membered heterocyclic compound with alternating BH and NH groups. It is very similar in structure and physical properties to benzene, and is therefore graphically described as "inorganic benzene":



This interesting compound, first obtained in 1926, has attracted the attention of numerous investigators. After a comparatively short period, methods of synthesis of borazole and its various derivatives were discovered, and their physical and chemical properties were quite widely studied. The chemistry of borazole has made particular progress during recent years.

Borazole compounds are interesting, not only theoretically, but also from a practical point of view. Thanks to the comparative stability of the borazole ring to oxidising and hydrolysing agents, various borazole derivatives, such as the hydroxy and amino derivatives, and especially those containing unsaturated hydrocarbon groups, can be used for the synthesis of boron-containing polymers possessing resistance to oils and high thermal stability. Borazole derivatives are also of interest as fuel for rocket motors.

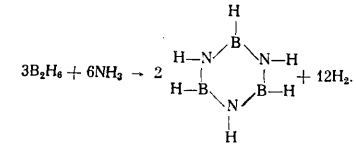
Achievements in the field of the chemistry of borazole were reviewed by Wiberg in 1948[1]. Several problems of the chemistry of borazole were dealt with by Schlesinger and Burg[2], Bauer[3], Stone[4], Zhigach and Kochneva[5], and Mikhailov[6], in reviews on the hydrides of boron, their nitrogen derivatives, and organic compounds of boron. The present paper is a complete review of the literature on borazole which has appeared up to 1958 and, in part, in 1959. All existing methods for synthesising borazole and its derivatives are reported and their value for preparative purposes is assessed.

The synthetic methods are divided into two groups. The first group comprises methods of forming the borazole ring, and the second includes methods based on reactions of functional derivatives of borazole. The second section also includes an account of the most important properties of borazole compounds, enabling valuable interconversions between certain borazole derivatives and others to be accomplished methodically. The general chemical characteristics of borazole compounds are given at the end of the paper.

I. METHODS OF SYNTHESIS OF BORAZOLE AND ITS DERIVATIVES

1. Synthesis from Diborane and its Alkyl Derivatives

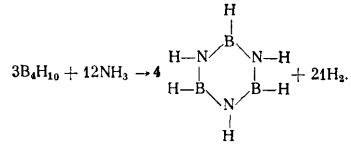
Stock and Pohland[7], in 1926, found that on heating a mixture of diborane and ammonia, or the addition compound $B_2H_6.2NH_3$, at 180°–190° in a sealed tube borazole in 33% yield was formed:



The structure of borazole as a plane six-membered ring with symmetry D_{3h} was established by electron diffraction[8,9].

Subsequently Schlesinger et al.[10] somewhat increased the yield of borazole (to 41%) in this method by raising the temperature to 200°. The reaction is complicated by the formation of a solid polymeric product $(BNH_n)_x$, the elementary composition of which varies with the experimental conditions[11].

Borazole is formed in the same yield by the action of ammonia on tetraborane[12]:

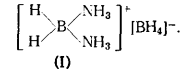


It is obtained also by the action of ammonia on B_5H_{11}.[7]

The mechanism of the formation of borazole from diborane and ammonia still remains obscure. It is suggested that at a high temperature an addition compound of borine and ammonia $BH_3.NH_3$ is formed, which then loses a molecule of hydrogen and is converted into aminoborine $BH_2–NH_2$, the latter by eliminating two hydrogen atoms forming BH=NH, which polymerises to borazole. The general scheme for the formation of borazole proposed by Wiberg and Bolz[11] is represented as follows:

$$3B_2H_6 + 6NH_3 \rightarrow 6H_3B \cdot NH_3 \xrightarrow{-3H_2} 6H_2B{-}NH_2 \xrightarrow{-3H_2} 6HB{=}NH \rightarrow 2B_3N_3H_6.$$

None of the stages has any experimental proof, and the scheme is purely speculative. It is now known that the primary product of the interaction of diborane and ammonia, "diborane diammoniate", $B_2H_6.2NH_3$, is not a dimer of $BH_3.NH_3$[14] but has the structure (I)[16–19]. It is difficult to explain how thermal decomposition of the complex compound (I) can produce a moderate yield of borazole.



(I)

N-Alkylated derivatives of borazole can be obtained starting from diborane. Schlesinger et al.[10] found that *N*-trimethylborazole is formed on heating a mixture of diborane and methylamine, the yield reaching 90% when the components are heated at 180°–200° for 2 h. If, however, a mixture of diborane, ammonia, and methylamine is heated, borazole and its *N*-methylated derivatives are obtained in proportions depending on those of the original reactants[10]: the main product is *N*-methylborazole when equimolar proportions of ammonia and methylamine are taken.

The process can be represented by the general equation

$$3B_2H_6 + 2x\,CH_3NH_2 + 2(3-x)\,NH_3 = 2B_3N_3H_{6-x}(CH_3)_x + 12H_2.$$

Alkyldiboranes also react with ammonia and amines at 190°–200°. Ammonia reacts with methyldiborane[21] or dimethyldiborane[21,22] to form small amounts of borazole, *B*-methyl-, *B*-dimethyl-, and *B*-trimethylborazoles, and also dimethylaminoborine, $(CH_3)_2NBH_2$.

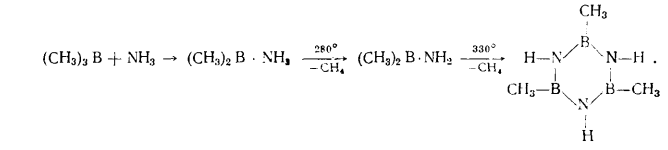
The preparation of borazole and its alkyl derivatives from diborane is very laborious and is of no practical value.

2. Synthesis from Boron Trialkyls

A second source of borazole derivatives is provided by boron trialkyls.

Wiberg et al.[20] obtained *B*-trimethylborazole by heating an equimolar mixture of trimethylboron and ammonia at 530° for 2 h: an "ammoniate" of trimethylboron is formed in the first stage of the reaction, and this at 280° can split off a molecule of methane and change into amino(dimethyl)-borine.

This latter compound is converted into *B*-trimethylborazole with elimination of methane at 330°:

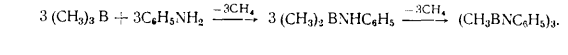


Similarly, *B*-triethylborazole is obtained in 80% yield by heating the ammonia compound of triethylboron in an autoclave at 450°[23].

The conversion of trimethylboron into borazole derivatives occurs on heating not only with ammonia but also with primary amines, though the latter require a higher temperature[24]. If the methylamine complex of trimethylboron is heated in a sealed tube at 310° for 1½ h, it is practically completely converted into dimethyl(methylamino)borine: *B*-trimethyl-*N*-trimethylborazole was obtained in 70% yield by heating this compound at 450° for 3 h.

Wiberg and his collaborators[20,24] consider that the conversion of amino(dimethyl)borine or dimethyl(methylamino)-borine into methyl derivatives of borazole takes place by their unimolecular decomposition into methane and imino-(methyl)borine, $CH_3B{=}NH$, or methyl(methylimino)borine, $CH_3B{=}NCH_3$, with subsequent trimerisation of the latter. However, no experimental data are at present available to support this mechanism.

Wiberg and Hertwig[25] studied also the reaction between trimethylboron and aniline, and concluded that heating the complex of these two compounds at 310° yields dimethyl-(phenylamino)borine, $(CH_3)_2BNHC_6H_5$, and the more volatile compound methyl(phenylimino)borine, $CH_3B{=}NC_6H_5$, which does not trimerise to *N*-triphenylborazole. They regarded this investigation as very important, supposing it to prove the existence of compounds having a double bond between boron and nitrogen atoms (so-called "borazines" in Wiberg's nomenclature) and thus supporting the mechanism of the formation of borazole and its derivatives by trimerisation of compounds of this type. However, their results relating to the preparation of methyl(phenylimino)borine, $CH_3B{=}NC_6H_5$, are incorrect. Confining themselves to measuring the vapour pressure of one of the fractions obtained in an experiment, they mistook for methyl(phenylimino)borine a mixture of aniline and dimethyl(phenylamino)borine, which have similar vapour pressures. Later Becher and Frick[26] showed that, if trimethylboron and aniline are heated at a higher temperature (at 375° for 15 h), the dimethyl(phenylamino)borine formed initially is converted into *B*-trimethyl-*N*-triphenylborazole:



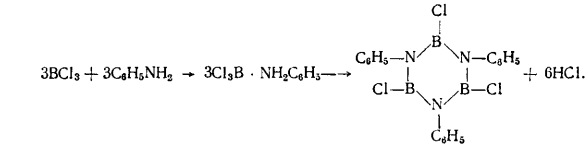
Dimethylboron fluoride also reacts with methylamine, eliminating the methyl groups to form *B*-trifluoro-*N*-trimethylborazole[27].

3. Synthesis from Boron Trichloride

Convenient methods for the preparation of borazole derivatives have been developed on the basis of boron trichloride.

Rideal[28], as early as 1889, investigated the reaction between BCl_3 and aniline, obtaining a substance giving an analysis corresponding to *B*-trichloro-*N*-triphenylborazole: he had synthesised the first compound of the borazole series, but did not establish its structure.

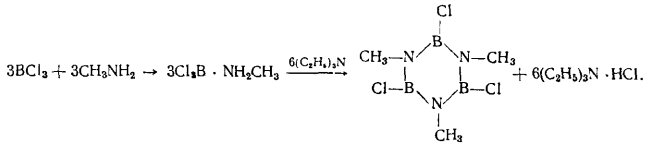
Fifty years later Jones and Kinney[29] studied this reaction in greater detail and found that addition of an equimolar quantity of aniline to a cooled solution of boron trichloride in benzene yields a complex compound which is converted into *B*-trichloro-*N*-triphenylborazole in 30% yield when the reaction mixture is subsequently boiled:



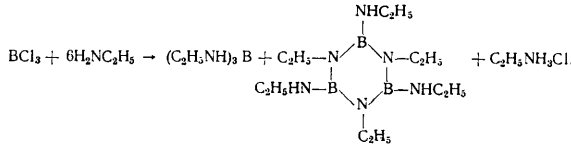
Similarly, *B*-trichloro-*N*-tri-*p*-tolylborazole[30] and *B*-trichloro-*N*-tri(*p*-methoxyphenyl)borazole[31] have been synthesised from BCl_3 and the appropriate amines. Groszos and Stafiej[32] raised the yield of *B*-trichloro-*N*-triphenylborazole to 73% by using toluene as solvent.

It is not yet possible to obtain borazole derivatives from equimolar quantities of BCl_3 and aliphatic amines. Wiberg and Hertwig[24] reported the preparation of *B*-trichloro-*N*-trimethylborazole by heating an equimolar mixture of BCl_3 and methylamine to 250°, but their product, which was not analysed, melted at 285°, whereas *B*-trichloro-*N*-trimethylborazole melts at 155°.

Borazole compounds can be obtained from BCl_3 and aliphatic amines in various ways. Thus a complex of boron trichloride and methylamine is first obtained by mixing the reactants in benzene solution; then triethylamine (2 moles) is added, and the reaction mixture boiled for 1½ h to give a 63% yield of *B*-trichloro-*N*-trimethylborazole[33]:

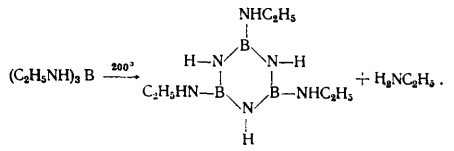


Recently Lappert[34] has found that BCl_3 (1 mole) reacts with ethylamine (6 moles) in pentane solution at -80° to yield, when the reaction products are subsequently distilled off, trisethylaminoborine (55%) and *B*-trisethylamino-*N*-triethylborazole:

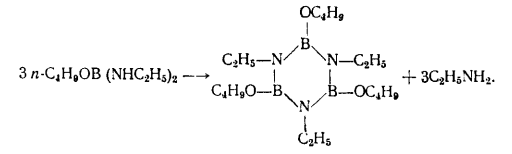


On heating the trisethylaminoborine at 200° for 3½ h,

Lappert obtained *B*-trisethylaminoborazole[34] in high yield:



He obtained[34] *B*-tributoxy-*N*-triethylborazole by pyrolysis of butoxy bis(ethylamino)borine or dibutoxy(ethylamino)-borine:

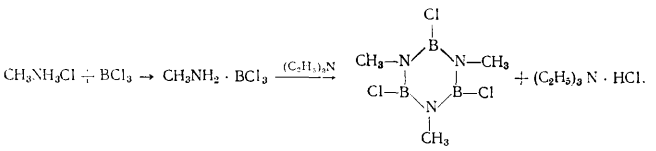


Brown and Laubengayer[35] made the interesting observation that under certain conditions boron trichloride can react with ammonium chloride to form *B*-trichloroborazole, this synthesis being accomplished in two ways. The first method consists in passing a stream of BCl_3 through ammonium chloride heated to 165°–175° in a tube. The second, simpler, method is to boil a mixture of chlorobenzene and ammonium chloride in the presence of BCl_3 vapour. In both cases the yield is 35%:

$$3NH_4Cl + 3BCl_3 \rightarrow (ClB{-}NH)_3 + 9HCl.$$

The yield of *B*-trichloroborazole can be considerably increased by treating the solid residue obtained from the previous experiment with the initial reactants[36]. The reaction is catalysed by mercury[33]. To obtain a large quantity of *B*-trichloroborazole, it is useful to employ rather more BCl_3 than is recommended by Brown and Laubengayer. The highest yield (43%) of *B*-trichloroborazole is obtained by adding BCl_3 to a suspension of NH_4Cl in chlorobenzene at a rate of 40 ml/h[33].

Hydrochlorides of primary aliphatic amines also react with BCl_3. Becher and Frick[26] obtained *B*-trichloro-*N*-trimethylborazole by Brown and Laubengayer's method from methylamine hydrochloride and BCl_3 in benzene solution. The product was purified by sublimation, but was not characterised. Turner and Warne[37] found that BCl_3 reacts with methylamine hydrochloride in benzene to form a complex $BCl_3.CH_3NH_2$, which is smoothly converted into *B*-trichloro-*N*-trimethylborazole and triethylamine hydrochloride on treatment in the cold with triethylamine:



Ethylamine and butylamine yielded with BCl_3 *B*-trichloro--*N*-triethylborazole and *B*-trichloro-*N*-tributylborazole respectively[37].

Brown and Laubengayer's method has been used to synthesise *B*-tribromoborazole by heating a mixture of ammonium bromide and boron tribromide in bromobenzene at 120°–130° for 8–12 h[36].

Borazole derivatives can be obtained starting from hydrohalides of hydrazine or an alkylhydrazine and BCl_3 or BBr_3.[38]

The mechanism of the formation of *B*-trichloroborazoles from ammonium salts and BCl_3 has not been discussed in the literature. Ammonium (or alkylammonium) tetrachloroborates are evidently formed in the first stage of the reaction, and on heating decompose into ammoniates or aminates of boron trichloride and HCl:

$$RNH_3Cl + BCl_3 \rightarrow NH_3R\,[BCl_4]^- \xrightarrow{-HCl} BCl_3 \cdot NH_3R.$$

This view of the reaction mechanism is supported by the infra-red absorption spectra of the reaction products formed by BCl_3 with amine salts, which have characteristic absorption bands in common with the spectra of potassium tetrachloroborate[39].

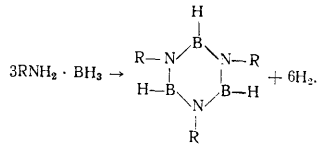
4. Synthesis from Ammonium Salts and Lithium Tetrahydroborate

A general method for obtaining borazole compounds is provided by the reaction between lithium tetrahydroborate and ammonium chloride or hydrochlorides of primary aliphatic amines, discovered by Schaeffer and Anderson[40].

To prepare *N*-trimethylborazole by this method an ethereal solution of methylamine hydrochloride and lithium tetrahydroborate is allowed to stand until hydrogen evolution ceases, and is then boiled for 3 h, the ether is distilled off, and the residue heated at 250°[40]. This technique was later simplified and applied to the preparation not only of *N*-trimethylborazole but also of other *N*-alkyl derivatives of borazole[41]. The reaction is carried out in two stages. An addition compound of borine and the amine, $BH_3.NH_2R$, is first obtained from the amine salt and $LiBH_4$ in ethereal solution at room temperature:

$$RNH_3Cl + LiBH_4 \rightarrow RNH_2 \cdot BH_3 + H_2 + LiCl,$$

and this is then decomposed at 250°–325°:



The *N*-triethyl-, *N*-tripropyl-, and *N*-triisopropylborazoles have been obtained in this way in 84–94% yield.

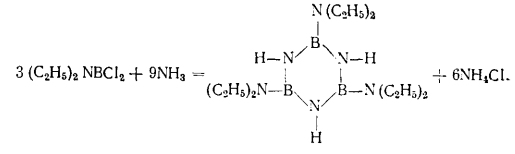
To obtain borazole, a mixture of $LiBH_4$, NH_4Cl, and broken glass is heated at 300° for 30 min[42]. The fairly low yield of borazole (30–35%) is explained by the fact that at high temperatures part of the borazole reacts with the original ammonium chloride to form *B*-chloroborazole. This method of preparing borazole has been improved and studied in detail by Mikheeva and Markina[43].

N-Triphenylborazole also has been synthesised by Schaeffer and Anderson's method[26].

5. Synthesis from *N*-Substituted Aminoboron Dichlorides

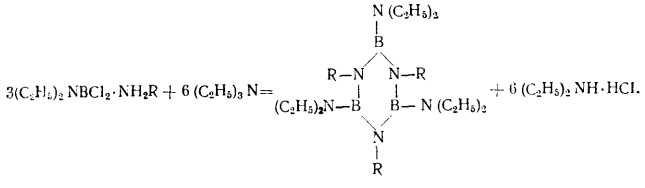
Niedenzu and Dawson[33] have synthesised *N*-substituted *B*-triaminoborazoles by the reaction of ammonia or primary amines with *N*-substituted aminoboron dichlorides. *B*-Tris-diethylaminoborazole is formed in 52% yield by the interaction of diethylaminoboron dichloride with ammonia in

benzene solution at a low temperature:



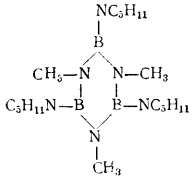
The reaction with primary amines can be conveniently carried out in two stages: a complex of diethylaminoboron dichloride with the amine is first obtained in ether, and this then reacts with triethylamine:

$$(C_2H_5)_2NBCl_2 + RNH_2 = (C_2H_5)_2NBCl_2 \cdot NH_2R$$



A 92% yield of *B*-tris(diethylamino)-*N*-trimethylborazole from diethylaminoboron dichloride and methylamine was obtained in this way, whereas the action of an excess of methylamine on diethylaminoboron dichloride gave only a 58% yield.

Similarly, *B*-tripiperidino-*N*-trimethylborazole is obtained from piperidinoboron dichloride, methylamine, and triethylamine:

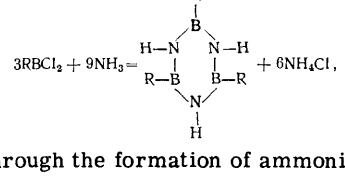


6. Synthesis from Alkyl- and Arylboron Dichlorides

A very simple and convenient method for the preparation of various alkyl and aryl derivatives of borazole is based on the use of organoboron dichlorides.

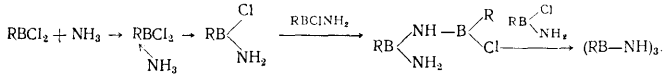
Mikhailov and Kostroma obtained a very good yield of *B*-triphenylborazole by passing ammonia into a heated benzene solution of phenylboron dichloride[44]: *B*-tri-*p*-tolyl-, *B*-tri-*p*-chlorophenyl-, and *B*-tri-*p*-bromophenylborazoles were similarly synthesised from the corresponding arylboron dichlorides[45].

The action of ammonia on isopentylboron dichloride yields *B*-triisopentylborazole[46], the reaction, expressed by the general equation



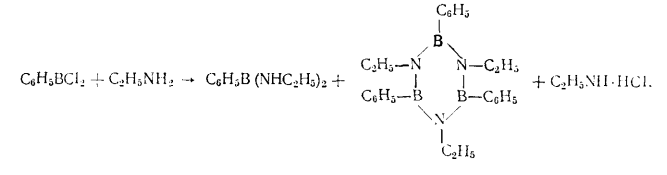
proceeding through the formation of ammoniates of the organoboron dichlorides.

The subsequent course of the reaction is probably essentially a conversion of the ammoniates into the alkyl or aryl(amino)boron chloride, the molecules of which then condense together to form *B*-trisubstituted borazole derivatives:

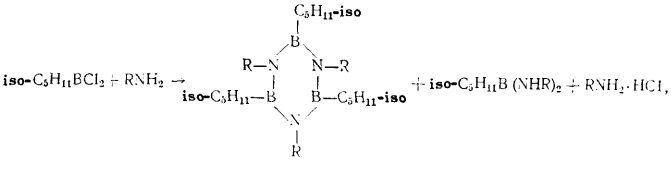


Booth and Kraus[47] obtained a substance having b.p. 100° at 0.005 mm/Hg by the action of ammonia and sodium on dibutylboron chloride, which they regarded as a polymer of butyl(imino)borine $(C_4H_9B{=}NH)_n$. This substance is not *B*-tributylborazole, since it has a higher boiling point even than *B*-triisopentylborazole[46] (115.5°/0.1). Ruigh and Gunderley[48] repeated the experiment of Booth and Kraus without using sodium, and obtained *B*-tributylborazole, but they do not give its physical properties.

The reaction between arylboron dichlorides and primary aliphatic amines is more complex. Thus ethylamine reacts with phenylboron dichloride to give a low (21%) yield of *B*-triphenyl-*N*-triethylborazole and a product in which both chlorine atoms have been replaced by alkylamino groups, namely bisethylamino(phenyl)borine (33%)[49]:



The reaction between primary aliphatic amines and alkylboron dichlorides occurs similarly, but borazole compounds are obtained in greater yield[46]. Thus ethylamine and isobutylamine react with isopentylboron dichloride to form *B*-triisopentyl-*N*-triethylborazole and *B*-triisopentyl-*N*-triisobutylborazole respectively in 50% yield, whereas the yield of the corresponding *N*-substituted diamino(isopentyl)borines amounts to 32–38%:



where R = C_2H_5, iso-C_4H_9.

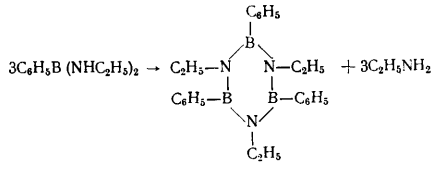
It is not possible to obtain *B*-trialkyl-*N*-triarylborazoles or *B*-triaryl-*N*-triarylborazoles directly by this method, since aromatic amines (aniline) form only *N*-substituted alkyl or aryl(diamino)borines with arylboron dichlorides[49] or alkylboron dichlorides[46]:

$$RBCl_2 + 4C_6H_5NH_2 = RB(NHC_6H_5)_2 + 2C_6H_5NH_2 \cdot HCl.$$

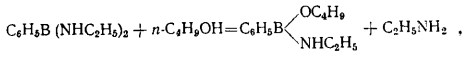
7. Synthesis from *N*-Substituted Alkyl and Aryl(diamino)borines

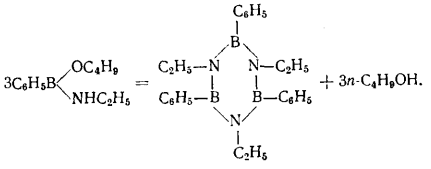
To synthesise alkyl and aryl derivatives of borazole we can use *N*-substituted alkyl- or aryl(diamino)borines formed by the action of primary amines on alkyl- or arylboron dichlorides.

Mikhailov and Aronovich[49] prepared *B*-triphenyl-*N*-triethylborazole by heating bisethylamino(phenyl)borine at 210° for 2 h:



The reaction is complicated by side reactions, and the yield is only 17%. Later it was found that the yield of *B*-triphenyl-*N*-triethylborazole can be raised to 85% if bisethylamino(phenyl)borine is heated at 260° in the presence of a small amount of n-butyl alcohol[50], which acts catalytically by forming with the original substance an aryl(ethylamino)-boric ester, which is smoothly converted into the borazole compound with elimination of the alcohol. The regenerated alcohol reacts afresh with the original organoboron amine:

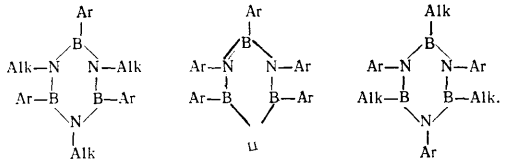




Phenylbisphenylaminoborine on heating at 270° forms hexaphenylborazole in 32% yield.

N-Arylated diamino(alkyl)borines require to be heated to a higher temperature (300°–360°). Pyrolysis of isopentylbisphenylaminoborine gives a high yield of *B*-triisopentyl-*N*-triphenylborazole[46].

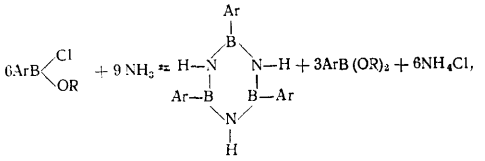
This method thus enables the following types of borazole derivatives to be prepared:



8. Synthesis from Arylchloroboric Esters

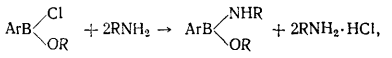
Mikhailov and Kostroma[44,50] have found that borazole derivatives can be obtained by the action of ammonia or amines on arylchloroboric esters.

When NH_3 is passed into an ethereal solution of the ester, the following reaction occurs:

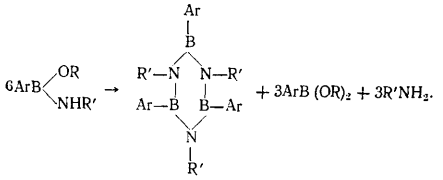


the yield of *B*-triarylborazoles being 83–87% on the basis of this equation. *B*-Triphenyl-, *B*-tri-*p*-tolyl-, and *B*-tri-α-naphthylborazoles have been synthesised in this way.

Primary aliphatic amines form aryl(alkylamino)boric esters,

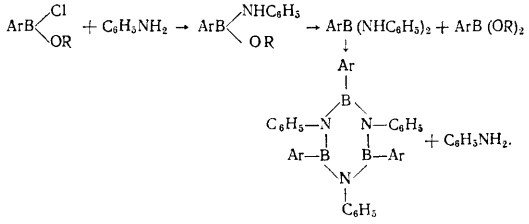


which on heating eliminate the alcohol and are converted into *B*-triaryl-*N*-trialkylborazoles:



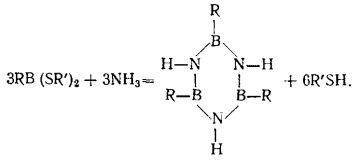
Under the influence of the resulting alcohol, half of the original amino ester is converted into an arylboric ester and the corresponding amine.

With aniline, aryl(phenylamino)boric esters are formed which on heating (200°) symmetrise into arylboric esters and *N*-phenylated diamino(phenyl)borines. The latter, as already indicated above, give on heating to 270°–400° a 30–35% yield of hexaarylborazoles:



9. Synthesis from Organothioboric Esters

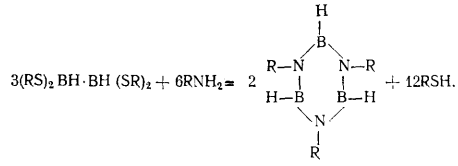
Mikhailov et al.[51] have found a simple and general method for preparing borazole derivatives in the reaction between esters of alkyl- or arylthioboric acids and ammonia, enabling *B*-trialkyl- and *B*-triarylborazoles to be prepared in yields of 85–95%:



10. Synthesis from Tetraalkylthiodiboranes

A convenient method of obtaining *N*-alkylated borazoles, discovered by Mikahilov and Shchegoleva[52], is the action of

primary amines on tetralkylthiodiboranes at room temperature:



N-Triethyl- and *N*-tributylborazoles have been synthesised by this method in yields of 66–77%.

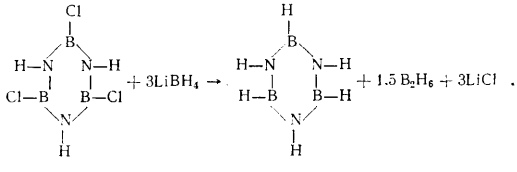
II. SYNTHETIC METHODS BASED ON REACTIONS OF FUNCTIONAL DERIVATIVES OF BORAZOLE

The investigation of the chemical properties of several compounds has led to the development of synthetic methods based on reactions of functional derivatives of borazole.

1. Synthesis of Borazole and its Derivatives from *B*-Chlorinated Borazoles

The study of the chemical properties of *B*-chlorinated borazoles has shown that the chlorine atoms are reactive, and can be displaced by hydrogen and various radicals.

Schaeffer et al.[36] found that all three chlorine atoms are replaced by hydrogen in the reaction of lithium tetrahydroborate with *B*-trichloroborazole in dibutyl ether:



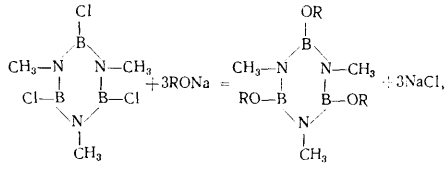
This reaction enables large quantities to be prepared with a 65% yield.

Reduction of *B*-trichloro-*N*-triphenylborazole with lithium tetrahydroaluminate in ethereal medium gives an 85% yield of *N*-triphenylborazole[53].

The possibility of obtaining borazole derivatives by reducing its *B*-trichloro derivatives with lithium tetrahydroborate was pointed out by Hohnstedt and Haworth[54], but no experimental details were given.

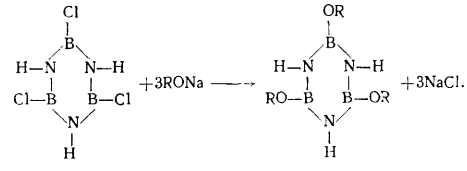
It is possible to replace chlorine atoms by hydroxy groups in a few cases. Thus *B*-trichloro-*N*-triphenylborazole[29] and *B*-trichloro-*N*-tri-*p*-methoxyphenylborazole[31] react with three molecules of water to form the corresponding *B*-trihydroxy derivatives, whereas the analogous *B*-trichloro-*N*-tri-*p*-tolylborazole is decomposed by moist benzene[30].

The *B*-alkoxy and *B*-phenoxy derivatives of borazole cannot be obtained by the action of alcohols or phenol on *B*-trichloro-*N*-trimethylborazole[55], methylamine hydrochloride and an alkyl or phenyl borate being formed. However, the chlorine atoms in this borazole compound can be replaced by alkoxy or phenoxy groups comparatively smoothly (in 43–58% yield) by the action of alcoholates of primary alcohols or a phenate in benzene solution. With alcoholates of secondary or tertiary alcohols, the yield of *B*-trialkoxy-*N*-trimethylborazoles is only 14–20%:



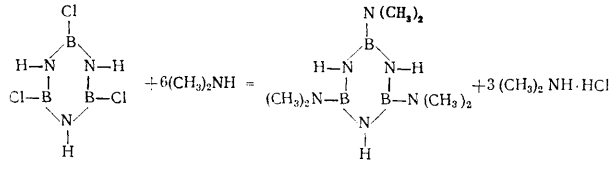
where R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, t-C_4H_9, C_6H_5.

Haworth and Hohnstedt[56] replaced the chlorine atoms in *B*-trichloroborazole by alkoxy groups by means of alcoholates. Thus sodium methylate reacts with *B*-trichloroborazole in boiling chlorobenzene to give a 54% yield of *B*-trimethoxyborazole, and with sodium ethylate *B*-triethoxyborazole is formed:

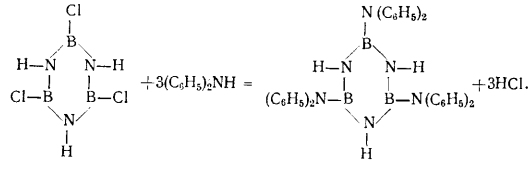


The chlorine atoms in *B*-trichloroborazole can be exchanged for alkylamino groups by the action of primary and secondary amines.

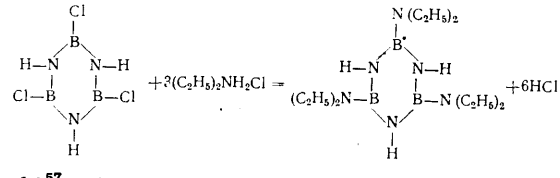
Gould[57] prepared *B*-tris(dimethylamino)borazole by the action of an excess of dimethylamine on *B*-trichlorborazole:



With diphenylamine the reaction can be carried out with the reactants in stoichiometric proportions[33]:



The chlorine atoms in *B*-trichloroborazole can be exchanged for diethylamino groups also by heating with diethylamine hydrochloride in tetrahydrofuran, but the yield of the resulting *B*-tris(diethylamino)borazole is low:

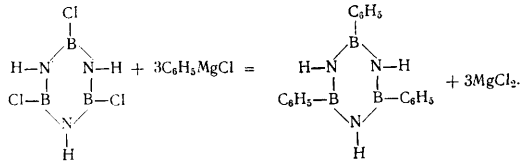


Gould[57] points out that *B*-trichloroborazole reacts with liquid ammonia to form *B*-triaminoborazole, but the properties of this compound are not given.

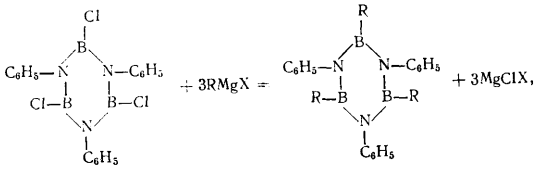
B-Trichloroborazole can react with diazomethane, yielding *B*-trischloromethylborazole[58].

B-Trichloro derivatives of borazole react with Grignard reagents.

Becher and Frick[26] synthesised *B*-triphenylborazole by the action of phenylmagnesium chloride on *B*-trichloroborazole. They obtained also *B*-triphenyl-*N*-trimethylborazole from *B*-trichloro-*N*-trimethylborazole and phenylmagnesium chloride:

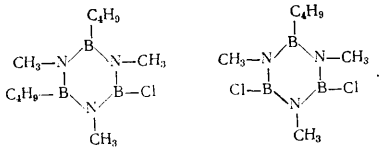


Groszos and Stafiej[32] synthesised various derivatives of borazole from *B*-trichloro-*N*-triphenylborazole and organomagnesium compounds, achieving yields of 65–84%. The yield of hexaphenylborazole is considerably worse with phenyllithium than with phenylmagnesium bromide:



where R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, iso-C_4H_9, C_6H_5, $CH_2{=}CH{-}CH_2$.

Exchange of chlorine atoms for alkyl groups occurs smoothly by reaction of Grignard reagents with *B*-trichloro-*N*-trimethylborazole. Ryschkewitsch et al.[59] synthesised *B*-triethyl-, *B*-triallyl-, and *B*-tributyl-*N*-trimethylborazole in this way. They found that when butylmagnesium chloride (2 moles) acts on *B*-trichloro-*N*-trimethylborazole (1 mole), the fully alkylated product is accompanied by the products of partial substitution, *B*-dibutyl-*B*-chloro-*N*-trimethylborazole and *B*-butyl-*B*-dichloro-*N*-trimethylborazole:

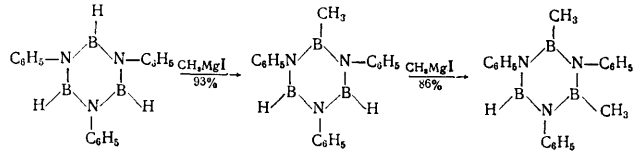


2. Synthesis of Borazole Derivatives from *N*-Alkyl and *N*-Aryl Borazoles

Smalley and Stafiej[53] made the interesting discovery that the hydrogen atoms in *N*-substituted borazoles are replaceable by alkyl or aryl groups by reaction with organomagnesium or organolithium compounds.

The action of three moles of the organometallic compound on one mole of *N*-triphenylborazole produced high yields of *B*-trimethyl-, *B*-tributyl-, and *B*-triphenyl-*N*-triphenylborazole. *B*-Alkylation of *N*-trimethylborazole yielded hexamethylborazole (83%). Yields of 49–61% of *B*-triphenyl-*N*-trimethylborazole were obtained by the action of phenyllithium or of phenylmagnesium bromide on *N*-trimethylborazole.

Replacement of hydrogen atoms in *N*-trisubstituted borazole can be carried out in stages, the action of 1 mole of CH_3MgI on *N*-triphenylborazole giving a 93% yield of *B*-methyl-*N*-triphenylborazole, which is smoothly converted by a second mole of CH_3MgI into *B*-dimethyl-*N*-triphenylborazole. Similar results are obtained by using phenylmagnesium bromide.



Stepwise replacement of hydrogen atoms can be accomplished also in *N*-trimethylborazole.

Partial substitution products can be used to synthesise derivatives having different groups linked to the boron atoms. For example, Smalley and Stafiej prepared *B*-methyl-*B*-ethyl-*B*-propyl-*N*-triphenylborazole by the following series of reactions:

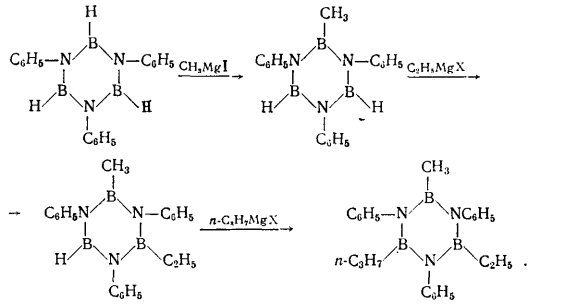


TABLE 1. Borazole and its alkyl derivatives.

Compound	B.p.	M.p.	n_D^{20}	d^{20}	Reference
Borazole	55	—58	1.3821	0.8419	7,11,36
B-Methylborazole	87[a]	—59			21
N-Methylborazole	84[a]				10
B-Dimethylborazole	107[a]	—48			21
N-Dimethylborazole	108[a]				10
B-Methyl-*N*-methylborazole	124[a]				10
$(CH_3B{-}NH)_3$	127	31.8			20,21
$(HB{-}NCH_3)_3$	134	—9	1.4404	0.8519	10,20,40,41
B-Dimethyl-*N*-methylborazole	139[a]				10
B-Trimethyl-*N*-methylborazole	158[a]				10
B-Methyl-*N*-trimethylborazole	162,5[a]				53
B-Dimethyl-*N*-trimethylborazole	187[a]				53
$(CH_3B{-}NCH_3)_3$	221	99			24,53
$(C_2H_5B{-}NH)_3$	67/7	—54			23
$(HB{-}NC_2H_5)_3$	68/20	—49.6	1.4384	0.8433	41,52
$(HB{-}NC_3H_7\text{-}n)_3$	225		1.4484	0.8347	41
$(HB{-}NC_3H_7\text{-}iso)_3$	203	—6.5	1.4443	0.8476	41
$(HB{-}NC_4H_9\text{-}n)_3$	80/0.25		1.4515	0.8426	52
$(iso\text{-}C_5H_{11}B{-}NH)_3$	115.5/0.1		1.4538	0.8485	46,51
$(C_2H_5B{-}NCH_3)_3$	98/1.8	2	1.4791[b]		59
$(n\text{-}C_4H_9B{-}NCH_3)_3$	140/1.1	—17	1.4759[b]		59
$(iso\text{-}C_5H_{11}B{-}NC_2H_5)_3$	114/0.06	45			46
$(iso\text{-}C_5H_{11}B{-}N{-}C_4H_9\text{-}n)_3$	128/0.06				46
$(CH_2{=}CH{-}CH_2B{-}NCH_3)_3$	112/1.3	—37	1.5047[b]		59
$(ClCH_2B{-}NH)_3$	125/0.01[c]	178			58

(a) By extrapolation of vapour-pressure data; (b) $n_D^{22.5}$; (c) temperature of sublimation.

TABLE 2. Alkyl-aryl borazole derivatives.

Compound	M.p., °C	Reference	Compound	M.p., °C	Reference
B-Methyl-*N*-triphenylborazole	142	53	$(CH_2{=}CH{-}CH_2B{-}NC_6H_5)_3$	99	32
B-Dimethyl-*N*-triphenylborazole	206	53	*B*-Methyl-*B*-ethyl-*N*-triphenylborazole	128	53
$(CH_3B{-}NC_6H_5)_3$	270	32, 53	*B*-Dimethyl-*B*-n-butyl-*N*-triphenylborazole	113	53
$(C_2H_5B{-}NC_6H_5)_3$	171	32	*B*-methyl-*B*-ethyl-*B*-n-propyl-*N*-triphenylborazole	131	53
$(n\text{-}C_3H_7B{-}NC_6H_5)_3$	171	32	$(C_6H_5B{-}NCH_3)_3$	249	26
$(iso\text{-}C_3H_7B{-}NC_6H_5)_3$	198	32	$(C_6H_5B{-}NC_2H_5)_3$	209	49, 50
$(n\text{-}C_4H_9B{-}NC_6H_5)_3$	132	32	$(p\text{-}CH_3C_6H_4B{-}NC_2H_5)_3$	221	50
$(iso\text{-}C_4H_9B{-}NC_6H_5)_3$	187	32	$(\alpha\text{-}C_{10}H_7B{-}NC_2H_5)_3$	271	44
$(iso\text{-}C_5H_{11}B{-}NC_6H_5)_3$ *	95.5	46			

* B.p. 181°/0.03.

TABLE 3. Aryl derivatives of borazole.

Compound	M.p., °C	Reference	Compound	M.p., °C	Reference
$(HB{-}NC_6H_5)_3$	161	26, 53	*B*-Phenyl-*N*-triphenylborazole	215	53
$(C_6H_5B{-}NH)_3$	182	26, 44, 51	*B*-Diphenyl-*N*-triphenylborazole	207	53
$(p\text{-}CH_3C_6H_4B{-}NH)_3$	190	44, 45	$(C_6H_5B{-}NC_6H_5)_3$	415	32, 49, 50
$(p\text{-}ClC_6H_4B{-}NH)_3$	270	45	$(p\text{-}CH_3C_6H_4B{-}NC_6H_5)_3$	284	50
$(p\text{-}BrC_6H_4B{-}NH)_3$	293	45			
$(\alpha\text{-}C_{10}H_7B{-}NH)_3$	187	44			

TABLE 5. Oxygen and nitrogen derivatives of borazole.

Compound	B.p., °C	M.p., °C	n_D	Reference
$(HOB{-}NC_6H_5)_3$		95—130		29
$(HOB{-}NC_6H_4OCH_3\text{-}p)_3$		112—120		31
$(CH_3OB{-}NH)_3$		111		56
$(C_2H_5OB{-}NH)_3$		54		56
$(CH_3OB{-}NCH_3)_3$	65/0.07		1.4610[a]	55
$(C_2H_5OB{-}NCH_3)_3$	80.5/0.1		1.4540[b]	55
$(n\text{-}C_3H_7OB{-}NCH_3)_3$	103/0.15		1.4561[c]	55
$(iso\text{-}C_3H_7OB{-}NCH_3)_3$	87/0.1		1.4460[d]	55
$(n\text{-}C_4H_9OB{-}NCH_3)_3$	134/0.3		1.4572[a]	55
$(n\text{-}C_4H_9OB{-}NC_2H_5)_3$	156/0.4		1.4544[e]	34
$(t\text{-}C_4H_9OB{-}NCH_3)_3$	125/0.52	87		55
$(C_6H_5OB{-}NCH_3)_3$	187/0.07	84		55
$(H_2NB{-}NH)_3$		85—105		57
$(CH_3NHB{-}NH)_3$		112		33
$[(CH_3)_2NB{-}NH]_3$				33, 57
$[(C_2H_5)_2NB{-}NH]_3$	150/7	>300		33
$[(C_6H_5)_2NB{-}NH]_3$		84		33
$[(C_2H_5)_2NB{-}NC_2H_5]_3$				33
$[(C_6H_5)_2NB{-}NC_2H_5]_3$	95/3			33
$(C_2H_5NHB{-}NC_2H_5)_3$	150/0.1		1.4826[f]	34

(a) n_D^{23}; (b) $n_D^{22.5}$; (c) n_D^{22}; (d) n_D^{23}; (e) n_D^{20}, d^{20} 0.935; (f) n_D^{20}, d^{20} 0.933.

The properties of borazole and its substitution products are listed in Table 1, those of its alkyl-aryl derivatives in Table 2, of its aryl derivatives in Table 3, of halogenated derivatives in Table 4, and the properties of oxygen and nitrogen derivatives of borazole are listed in Table 5.

TABLE 4. Halogenated borazole derivatives

Compound	B.p., °C	M.p., °C	Reference
B-Chloroborazole	109.5[a]	—34.6	42
B-Bromoborazole	122.3[a]	—34.8	42
B-Dichloroborazole	151.9[a]	33.5[a]	42
B-Dibromoborazole	167.1[a]	50	42
$(ClB{-}NH)_3$		84.5	33, 36
$(BrB{-}NH)_3$		128	36
$(FB{-}NCH_3)_3$	224	85	27
$(ClB{-}NCH_3)_3$	120—130/0.1—1[b]	155	37, 59
$(ClB{-}NC_2H_5)_3$		57	37
$(ClB{-}NC_4H\text{-}p)_3$[e]	120 0.5	~30	37
B-Di-n-butyl-*B*-chloro-*N*-trimethylborazole	122/1.13[c]		59
B-n-butyl-*B*-dichloro-*N*-trimethylborazole	101/1.1[d]	— 4	59
$(ClB{-}NC_6H_5)_3$		272	29
$(ClB{-}NC_6H_4CH_3\text{-}p)_3$		309	30
$(ClB{-}NC_6H_4OCH_3\text{-}p)_3$		235	31

(a) By extrapolation of vapour-pressure data.
(b) Sublimation temperature.
(c) $n_D^{22.5}$ 1.4008.
(d) $n_D^{22.5}$ 1.4876.
(e) Probably $(ClB{-}NC_6H_4CH_3\text{-}P)_3$ (Ed. of Translation).

III. PROPERTIES OF BORAZOLE AND ITS DERIVATIVES

Stock and Pohland[7], on the basis of their experiments with a small quantity of gaseous borazole, considered it to be a stable compound, undergoing no changes in the course of several months. Schaeffer et al.[36] found, however, that borazole in the liquid state, even when kept at -80° for a few days, decomposed appreciably, traces of a colourless non-volatile precipitate separating out. When kept at room temperature for a few weeks, borazole evolves a considerable quantity of hydrogen together with a small amount of diborane and other volatile products. Borazole is more stable in the gaseous state.

Borazole and the majority of its derivatives react in air, and all manipulations with it are therefore carried out in dry nitrogen. The aryl derivatives of borazole possess the greatest stability in air. Thus, for example, *B*-triphenyl-*N*-triethylborazole and hexaphenylborazole can be kept in an open vessel for a long time[49].

Wiberg and Bolz[11] found that at room temperature borazole forms 1 : 3 molecular compounds with water, methyl alcohol, and HBr. According to their data, the methanol compound, imino(methoxy)borine, $CH_3OB{=}NH$, which represents a monomeric form of *B*-trimethylborazole. This statement of Wiberg and Bolz is incorrect. According to Haworth and Hohnstedt's results[56], the complex of borazole with three molecules of methanol evolves hydrogen on heating and is converted into the ammoniate of trimethyl borate $[(CH_3O)_3B.NH_3]$, *B*-trimethoxyborazole, and a non-volatile solid of indefinite composition. The latter workers found that with ethanol, borazole forms an adduct, $B_3N_3H_6 \cdot 3C_2H_5OH$, which is unstable and even at -30° is partly converted into NH_3, ethyl borate, and a solid, which at 100° is partly converted into *B*-triethoxyborazole.

NH_3, ethyl borate, and a solid, which at 100° is partly converted into *B*-triethoxyborazole.

According to Wiberg and Bolz[11] at 100° the complex compound of borazole with HBr splits off hydrogen and is converted into tribromoborazole, whereas the action of bromine on borazole yields dibromoborazole: the physical properties of these compounds were not described.

At room temperature borazole reacts with boron trichloride and tribromide forming the corresponding mono- and dihalogenated borazoles[42], hydrogen, and non-volatile solid products. Borazole reacts with amino(dimethyl)borine to form methane and mono-, di-, and trimethylborazoles[21].

At 100° borazole can react with trimethylboron, forming *B*-methyl-, *B*-dimethyl-, and *B*-trimethylborazoles[10].

The majority of borazole derivatives, like borazole itself, are hydrolysed on heating with water, methylboric acid and ammonia being formed from *B*-trimethylborazole, and boric acid, methylamine, and hydrogen from *N*-trimethylborazole[20]. Hexamethylborazole yields methylboric acid and methylamine on hydrolysis[24].

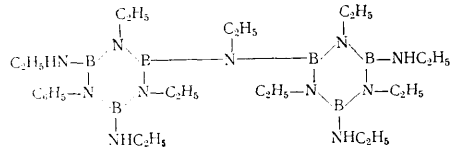
At 100° *B*-triphenyl-*N*-trimethylborazole is smoothly decomposed under the influence of water into methylamine and phenylboric acid[53], whereas under similar conditions *B*-trimethyl-*N*-triphenylborazole does not undergo any change[53].

At 45° *B*-trimethylborazole forms with hydrogen chloride a non-volatile, colourless, solid compound[20], which is regarded as a product of the addition of three molecules of HCl to the original compound[20]. According to Wiberg and Hertwig[24], hexamethylborazole at 90° forms with HCl an addition compound containing three molecules of HCl, but this compound was not identified analytically. At 150° hexamethylborazole is converted by HCl into methylboron dichloride and methylamine hydrochloride.

N-Methylborazole reacts at 100° with trimethylboron forming *B*-methyl-*N*-methyl-, *B*-dimethyl-*N*-methyl-, and *B*-trimethyl-*N*-methylborazoles, and hydrogen[10].

The ability of *N*-substituted derivatives of borazole to react with Grignard reagents, as well as the reactivity of *B*-halogenated borazoles, has been discussed in section II.

At 200° *B*-trisethylamino-*N*-triethylborazole eliminates ethylamine and is converted into a condensation product which has been given the following structure:



Further heating at 600° converts this product into a polymer, which is hydrolysed by hot water to boric acid and ethylamine[34].

B-Trimethoxyborazole reacts with methanol at 100° to form the ammoniate of trimethyl borate[56]. Pyrolysis of *B*-trimethoxyborazole yields traces of the ammoniate of trimethyl borate and a non-volatile solid[56].

Investigations have been made of the ultra-violet spectra of borazole[60,61], *B*-trimethyl-, *N*-trimethyl-, *B*-trichloro-[62], *B*-triphenyl-[63,64], *B*-tri-*p*-chlorophenyl-[64], *N*-triphenyl-, *B*-triphenyl-, and *B*-trimethyl-*N*-triphenylborazoles[63].

Studies have been made also of the infra-red spectra of borazole[26,65] and several of its derivatives: *B*-trimethylborazole[66] and *B*-triphenyl-, *N*-triphenyl-, *B*-trimethyl-*N*-triphenyl-, *B*-triphenyl-*N*-trimethyl-, *B*-trichloro-, *B*-trichloro-*N*-triphenyl-, and *B*-trichloro-*N*-trimethylborazoles[26].

The Raman spectra of borazole[65] and *B*-trimethylborazole[67] have been studied.

X-Ray and electron diffraction methods have been used to determine interatomic distances in borazole[9] (N–B bond length 1.44 Å), *B*-trichloroborazole[68-70] (1.41 Å), and *N*-trimethylborazole[70] (1.42 Å).

The heat of formation of *B*-trichloroborazole has been determined[71].

1. E. Wiberg, Naturwiss., 35, 182, 212 (1956).
2. H. Schlesinger and A. Burg, Chem. Rev., 31, 43 (1942).
3. S. Bauer, ibid., 31, 43 (1942).
4. F. Stone, Quart. Rev., 9, 174 (1955).
5. A. F. Zhigach and L. N. Kochneva, Uspekhi Khim., 25, 1267 (1956).
6. B. M. Mikhailov, ibid., 28, 1450 (1959).
7. A. Stock and E. Pohland, Ber., 59, 2215 (1926).
8. A. Stock and R. Wierl, Z. anorg. Chem., 203, 228 (1931).
9. S. Bauer, J. Amer. Chem. Soc., 60, 524 (1938).
10. H. Schlesinger and D. Ritter, ibid., 60, 1296 (1938).
11. E. Wiberg and A. Bolz, Ber., 73, 209 (1940).
12. A. Stock, E. Wiberg, and H. Martini, ibid., 63, 2427 (1930).
13. H. Schlesinger and A. Burg, J. Amer. Chem. Soc., 60, 290 (1938).
14. L. E. Agronomov, Zhur. Obshch. Khim., 9, 1389 (1939).
15. A. Burg, J. Amer. Chem. Soc., 69, 747 (1947).
16. D. Schultz and R. Parry, ibid., 80, 4 (1958).
17. S. Shore and R. Parry, ibid., 80, 8 (1958).
18. R. Parry and S. Shore, ibid., 80, 15 (1958).
19. S. Shore, P. Girardot, and R. Parry, ibid., 80, 20 (1958).
20. E. Wiberg, K. Hertwig, and A. Bolz, Z. anorg. Chem., 256, 177 (1948).
21. H. Schlesinger, L. Horwitz, and A. Burg, J. Amer. Chem. Soc., 58, 409 (1936).
22. H. Schlesinger, N. Flodin, and A. Burg, ibid., 61, 1078 (1939).
23. A. F. Zhigach, E. B. Kozakova, and E. S. Krongauz, Dokl. Akad. Nauk SSSR, 111, 1029 (1956).
24. E. Wiberg and K. Hertwig, Z. anorg. Chem., 255, 141 (1947).
25. E. Wiberg and K. Hertwig, ibid., 257, 138 (1948).
26. H. Becher and S. Frick, ibid., 295, 83 (1958).
27. E. Wiberg and G. Horeld, Z. Naturforsch., 6b, 338 (1951).
28. S. Rideal, Ber., 22, 992 (1889).
29. R. Jones and C. Kinney, J. Amer. Chem. Soc., 61, 1378 (1939).
30. C. Kinney and M. Kolbezen, ibid., 64, 1584 (1942).
31. C. Kinney and C. Mohoney, J. Org., 8, 526 (1943).
32. S. Groszos and S. Stafiej, J. Amer. Chem. Soc., 80, 1357 (1958).
33. K. Niedenzu and J. Dawson, ibid., 81, 3561 (1959).
34. M. Lappert, Proc. Chem. Soc., 59 (1959).
35. A. Laubengayer and C. Brown, Abstracts of Papers presented at the September Meeting of the American Chemical Society, 10 (1949); C. Brown and A. Laubengayer, J. Amer. Chem. Soc., 77, 3699 (1955).
36. R. Schaeffer, M. Steindler, L. Hohnsted, H. Smith, L. Eddy, and H. Schlesinger, J. Amer. Chem. Soc., 76, 3303 (1954).
37. H. Turner and R. Warne, Chem. and Ind., 526 (1958).
38. H. Emeleus and G. Videla, Proc. Chem. Soc., 288 (1957).
39. W. Kynaston and H. Turner, ibid., 304 (1958).
40. G. Schaeffer and E. Anderson, J. Amer. Chem. Soc., 71, 2143 (1949).

41. W. Hough, G. Schaeffer, M. Dzurus, and A. Stewart, ibid., 77, 864 (1955).
42. G. Schaeffer, R. Schaeffer, and H. Schlesinger, ibid., 73, 1612 (1951).
43. V. I. Mikheeva and V. Yu. Markina, Zhur. Neorg. Khim., 1, 2700 (1956).
44. B. M. Mikhailov and T. V. Kostroma, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1125 (1957).
45. B. M. Mikhailov, A. N. Blokhina, and T. V. Kostroma, Zhur. Obshch. Khim., 29, 1483 (1959).
46. B. M. Mikhailov and T. K. Kozminskaya, Dokl. Akad. Nauk SSSR, 121, 656 (1958).
47. R. Booth and C. Kraus, J. Amer. Chem. Soc., 74, 1415 (1952).
48. W. Ruigh and F. Gunderley, Chem. Eng. News, 34, 1994 (1956).
49. B. M. Mikhailov and P. M. Aronovich, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1123 (1957).
50. B. M. Mikhailov and T. V. Kostroma, Zhur. Obshch. Khim., 29, 1477 (1959).
51. B. M. Mikhailov, T. K. Kozminskaya, N. S. Fedotov, and V. A. Dorokhov, Dokl. Akad. Nauk SSSR, 127, 1023 (1959).
52. B. M. Mikhailov and T. A. Shchegoleva, ibid., 131, 843 (1960).
53. J. Smalley and S. Stafiej, J. Amer. Chem. Soc., 81, 582 (1959).
54. L. Hohnstedt and D. Haworth, Chem. Eng. News, 35, 67 (1957).
55. M. Bradley, G. Ryschkewitsch, and H. Sisler, J. Amer. Chem. Soc., 81, 2635 (1959).
56. D. Haworth and L. Hohnstedt, ibid., 81, 842 (1959).
57. J. Gould, U. S. Pat. 2754177 (1956).
58. H. Turner, Chem. and Ind., 1405 (1958).
59. G. Ryschkewitsch, J. Harris, and H. Sisler, J. Amer. Chem. Soc., 80, 4515 (1958).
60. J. Platt, H. Klevens, and G. Schaeffer, J. Chem. Phys., 15, 598 (1947).
61. L. Jacobs, J. Platt, and G. Schaeffer, ibid., 16, 115 (1948).
62. C. Rector, G. Schaeffer, and J. Platt, ibid., 17, 460 (1949).
63. H. Becher and S. Frick, Z. phys. Chem., 12, 241 (1957).
64. A. N. Nikitina, V. A. Vaver, N. S. Fedotov, and B. M. Mikhailov, Optika i Spektrosk., 7, 744 (1959).
65. B. Crawford and J. Edsall, J. Chem. Phys., 7, 223 (1939).
66. W. Price, R. Fraser, T. Robinson, and H. Longuet-Higgins, Discuss. Faraday Soc., No. 9, 131 (1950).
67. J. Goubeau and H. Keller, Z. anorg. Chem., 272, 303 (1953).
68. D. Coursen and J. Hoard, J. Amer. Chem. Soc., 74, 1742 (1952).
69. R. Pease, ibid., 74, 4219 (1952).
70. K. Coffin and S. Bauer, J. Phys. Chem., 59, 193 (1955).
71. E. Van Artsdalen and A. Dworkin, J. Amer. Chem. Soc., 74, 3401 (1952).

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DEVELOPMENT IN THE SYNTHESIS AND APPLICATION OF ION EXCHANGE AND ELECTRON EXCHANGE RESINS

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INTRODUCTION

The introduction of cross-linked polymeric electrolytes – ion exchange resins – has provided an entirely new approach to many problems of purification and separation of chemically similar substances, i.e. to the central problems of analytical and preparative chemistry. The first problems to be solved in this way concerned desalting or deionisation of industrial solutions, e.g. in the sugar industry, the production of drinking water from sea water, or the substitution of undesirable ions by acceptable ones, e.g. calcium and silicate in boiler water by sodium and hydroxide.

Problems such as these make very simple demands of an ion exchanger. Selectivity for a particular ion is not required. On the contrary the polymer must be a general purpose absorber of a wide range of ions.

Much more sophisticated problems arise in separating individual substances from complex natural or industrial products. The introduction of polymeric ion exchangers in conjunction with chromatographic methods has brought about a real revolution in this field. It should be remembered that while chromatography is an exceptionally selective method of separation, it is lengthy and comparatively inefficient in terms of unit volume or cross-section of the apparatus (ion-exchange columns). Ion exchange and chromatography are therefore best used in analysis and in small scale synthesis. The extraction and purification of rare, highly dispersed, and radioactive elements, and the separation of stable isotopes are the fields of industrial inorganic chemistry in which the use of ion exchange and chromatography is expedient. As far as the polymeric materials are concerned, the chief problem here is to make selective absorbents which have at least a group specificity, and preferably an individual specificity for given elements.

In the organic chemical industry the most important applications of ion exchange and chromatography are related to the production of valuable small-tonnage products of complex nature – antibiotics, vitamins, hormones, alkaloids, active protein preparations (antigens, antibodies, enzymes, viruses, baceteriophages). In these cases, the advantages of the ion exchange method are used to the full; it is the most "gentle" of all preparative methods, and enables particularly sensitive and labile organic compounds to be purified and concentrated. Applications of ion exchange in organic chemical technology make special demands on the synthesis of ion-exchange resins. As in the previous case, high selectivity for individual ions is involved. In addition, the large dimensions of organic ions, containing various functional groups, pose additional problems in the synthesis of resins suitable for their separation and purification.

The use of polymeric resins as reagents in chemical reactions is a new field of application that has emerged recently. Cations and anion-exchange resins are used successfully as catalysts in reactions requiring acidic or basic catalysts. Special electron-exchange resins, i.e. polymers able to undergo reversible oxidation-reduction, are used as reagents for the oxidation or reduction of a given material; contamination of the product by extraneous matter, which occurs when the usual oxidising and reducing agents are used, is thus avoided. These are the most important aspects of the applications of ion-exchange and electron-exchange resins.