

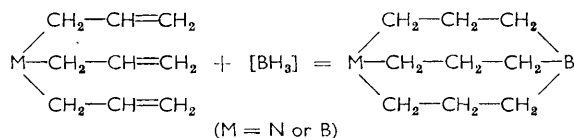
917. Heterocyclic Organoboron Compounds. Part II.¹ Preparation and Properties of 1-Aza-5-boratricyclo[3,3,3,0]undecane and Related Compounds.

By N. N. GREENWOOD, J. H. MORRIS, and J. C. WRIGHT.

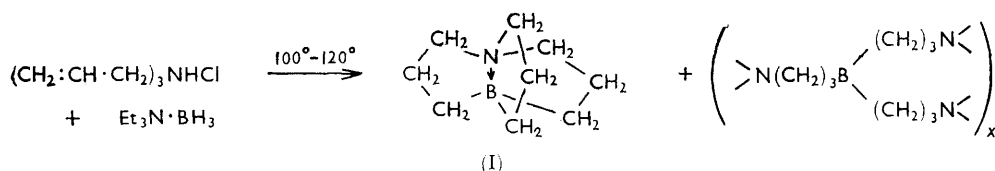
Hydroboration of the three double bonds in triallylamine yields a tricyclic compound (I) with bridgehead nitrogen and boron atoms and a direct B-N bond; it is an unreactive, volatile solid which hydrolyses slowly to dipropylaminopropylboronic acid (II) and tripropylamine. Hydroboration of triallylborane yields the analogous bicyclic dibora-compound (IV) which is highly reactive and forms adducts with nitrogen donors.

The infrared spectrum of azaboratricycloundecane is compared with those of triethanolamine borate and trisethyleneglycol diborate, and its boron and proton n.m.r. spectra are also elucidated.

THE formation of heterocyclic organoboranes in which three terminal olefinic groups are united to a single boron atom by means of the hydroboration reaction has not previously been reported.² It seemed possible that heterocyclic compounds with a bridgehead boron atom could be synthesized by this method, and this led to a study of the hydroboration of the triallyl derivatives of nitrogen and boron:



In preliminary experiments, triallylamine was treated with triethylamine-borane at several concentrations in a hydrocarbon solvent to yield mainly a polymeric material. During the course of the reaction about 10% of the product precipitated as a polymeric solid, and subsequent removal of solvent from the remaining solution left a viscous polymeric liquid from which only a trace of 1-aza-5-boratricyclo[3,3,3,0]undecane (I) could be isolated. In further experiments, triallylamine was first converted to the hydrochloride and then hydroboronated with triethylamine-borane in light petroleum to yield azaboratricycloundecane (I) and a polymeric material:



Presumably in the first reaction the electron-donor properties of the nitrogen atom in triallylamine interfered with hydroboration, since the non-bonding electrons on the nitrogen atom would compete with the π -electrons of the double bonds as a site for the electrophilic attack of the BH_3 unit.

Azaboratricycloundecane, m. p. 123° , was readily soluble in organic solvents, such as alcohol, acetone, carbon tetrachloride, carbon disulphide, and cyclohexane, and insoluble in water, although it was steam-volatile. It had a camphor-like smell and its vapour pressure (Table I) corresponded to the equation $\log P(\text{mm.}) = 8.743 - 2845/T$, from which the heat of vaporization is 13.02 kcal. mole⁻¹.

Molecular-weight measurements showed that azaboratricycloundecane was monomeric in the gas phase (Found 158. $\text{C}_9\text{H}_{18}\text{NB}$ requires 151). Cryoscopic measurements showed

¹ Part I, Greenwood and Morris, *J.*, 1960, 2922.

² Maitlis, *Chem. Rev.*, 1962, 62, 223.

TABLE 1.

Vapour pressure of 1-aza-5-boratricyclo[3,3,3,0]undecane.

t°	55.5	60.2	65.0	69.7	74.6	79.4	85.1
P (mm.) ...	1.00	1.54	2.13	2.78	3.67	4.85	6.56
t°	90.2	94.9	99.5	105.6	109.4	115.9	120.1
P (mm.) ...	7.93	10.14	12.53	17.27	20.37	27.30	31.43

the compound to be associated in non-polar solvents, and molecular weights of 825 and 981 by the Rast method indicate that it is approximately a hexamer under these conditions.

The infrared absorption spectrum between 400 and 4000 cm^{-1} is recorded in Table 2 and assignments are considered in the discussion.

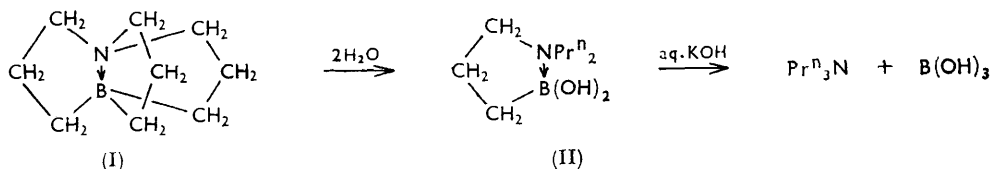
TABLE 2.

Infrared absorption spectrum of 1-aza-5-boratricyclo[3,3,3,0]undecane.

ν cm^{-1}	ϵ	Assignment	ν cm^{-1}	ϵ	Assignment
437	12		1135	200	$^{11}\text{B}-\text{C}_3$ antisym. stretch
478	17		1144	78	$^{10}\text{B}-\text{C}_3$ antisym. stretch
509	21		1162	17	CH_2 twist
568	64	Ring deformation	1215	55	CH_2 twist
660	66	$^{11}\text{B}-\text{C}_3$ sym. stretch	1250	36	CH_2 twist
668	sh	$^{10}\text{B}-\text{C}_3$ sym. stretch	1271	166	$\text{B}-\text{N}$ stretch
763	40	CH_2 rock	1305	36	CH_2 wag
788	30	CH_2 rock	1348	34	CH_2 wag
862	21		1355	sh	CH_2 wag
880	23		1429	53	NCH_2 scissors
900	55	$\text{N}-\text{C}_3$ sym. stretch	1452	62	BCH_2 scissors
932	13		1467	100	CCH_2 scissors
953	19		1472	sh	? CH_2 scissors
975	74	$\text{C}-\text{C}$ stretch	2819	160	NCH_2 sym. $\text{C}-\text{H}$ stretch
1000	36	?Ring vibration	2857	170	CCH_2 sym. $\text{C}-\text{H}$ stretch
1039	130	$\text{N}-\text{C}_3$ antisym. stretch	2879	200	BCH_2 sym. $\text{C}-\text{H}$ stretch
1082	45	?Ring vibration	2920	320	CCH_2 antisym. $\text{C}-\text{H}$ stretch
			2954	210	BCH_2 antisym. $\text{C}-\text{H}$ stretch

Boron-11 nuclear magnetic resonance showed a rather broad singlet at +8.89 p.p.m. from trimethylborate in carbon disulphide solution (-9.40 p.p.m. from boron trifluoride-diethyl ether in carbon tetrachloride solution). Proton nuclear magnetic resonance in carbon disulphide solution showed three multiplets: a triplet centred at 9.65 τ , a quintet centred at 8.40 τ , and a triplet centred at 7.37 τ relative to tetramethylsilane. The coupling constants and the symmetry of the triplets are discussed later.

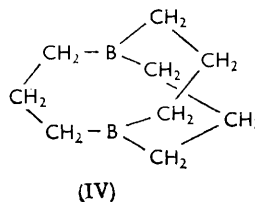
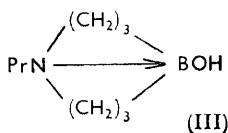
Azaboratricycloundecane was stable in air and towards peroxidic oxidizing agents. It failed to form adducts with ammonia or triethylphosphine, indicating that the boron and nitrogen were already internally co-ordinated. During its isolation by steam distillation, some hydrolysis occurred, yielding dipropylaminopropylboronic acid (II), and this could be further hydrolysed over a period of 24 hours with boiling aqueous alkali to yield tripropylamine, identified as the picrate. This hydrolysis presumably proceeds via the initial



partial dissociation of the $\text{B}-\text{N}$ bond at 100° followed by hydrolytic fission of the $\text{B}-\text{C}$ bond to yield the boronous acid (III) which, as expected, is unstable and undergoes further hydrolysis by the same mechanism to produce the boronic acid (II). This is consistent

with the behaviour of triethylborane, which does not react with cold water³ but is hydrolysed at 90—100°.⁴

Dipropylaminopropylboronic acid (II) could not be dehydrated to the corresponding boroxine $[\text{Pr}_2\text{N}(\text{CH}_2)_3\text{BO}]_3$ by the usual procedures. Its stability is related to the fact that the fourth orbital on boron is already involved in bonding to the nitrogen atom and is therefore not available for $p_\pi-p_\pi$ bonding with oxygen in the boroxine ring.



In an attempt to prepare diborabicycloundecane, $\text{B}[(\text{CH}_2)_3]_3\text{B}$, triallylborane was treated with triethylamine-borane; a polymer was obtained as previously reported.⁵ However, pyrolysis of this polymer yielded a mixture of at least eight volatile products which could be separated by gas-liquid chromatography. The major component of the mixture appeared to be 1,5-diborabicyclo[3,3,3]undecane (IV), since elemental analysis and molecular weight of the mixture corresponded approximately to that required for $\text{C}_9\text{H}_{18}\text{B}_2$. The compound, unlike its azaborane-analogue, was extremely sensitive to air, water, and ethanol, suggesting that the two boron atoms were 3-co-ordinate rather than 4-co-ordinate. It reacted with ammonia at -78° to form a 2:1 adduct, $(\text{NH}_3)_2\text{C}_9\text{H}_{18}\text{B}_2$, which dissociated completely into its components below 0° . Peroxidic hydrolysis of the pyrolysed product yielded 1,3-propanediol uncontaminated with 1,2-propanediol (infrared spectra) and protonolysis with anhydrous propionic acid⁶ gave propane in low yield together with small amounts of propylene and hydrogen. Infrared examination of the purified product showed no bands near 2400 cm^{-1} characteristic of B-H stretching absorptions,⁷ and no bands typical of either terminal olefins, or *cis*- or *trans*-CH=CH-groups.⁸

Two further model compounds were prepared to aid in the elucidation of the structure of azaboratricycloundecane and to aid in the assignment of its infrared and n.m.r. spectra, namely triethanolamine borate (VII, VIII) and trisethyleneglycol diborate (V, VI). Triethanolamine borate was prepared by heating boric acid and triethanolamine under vacuum to eliminate water.⁹ Its infrared spectrum, recorded between 375 and 3650 cm^{-1} is recorded in the Experimental section.

Trisethyleneglycol diborate was prepared by heating stoichiometric quantities of ethyleneglycol and boric acid at 50° under vacuum to yield the theoretical quantity of water and crude material which was purified by recrystallization and sublimation. The compound obtained in this way differed from that of Pictet and Geleznoff¹⁰ by being very soluble in dioxan, fairly soluble in carbon tetrachloride, benzene, and ethyleneglycol dimethyl ether, and slightly soluble in diethyl ether. The proton magnetic resonance spectrum at 60 Mc./sec. in methylene chloride showed two sets of peaks, a singlet at $+1.18\text{ p.p.m.}$ and a multiplet centred at $+1.43\text{ p.p.m.}$ from methylene chloride. The separation of the two major peaks of the multiplet was 2.4 c./sec. Under better resolution the singlet showed a shoulder on the low-field side, suggesting that there were more peaks here. From the results it is not

³ Frankland and Duppa, *Proc. Roy. Soc.*, 1859, **10**, 568.

⁴ Meerwein, Hinz, Majert, and Sönke, *J. prakt. Chem.*, 1937, **147**, 226.

⁵ Mikhailov and Pozdnev, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk.*, 1962, 1475.

⁶ Crichton, Holliday, Massey, and Thompson, *Chem. and Ind.*, 1960, 347.

⁷ Bellamy, Gerrard, Lappert, and Williams, *J.*, 1953, 2412.

⁸ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958.

⁹ Rojahn, *Chem. Zentr.*, 1933, **2**, 2704.

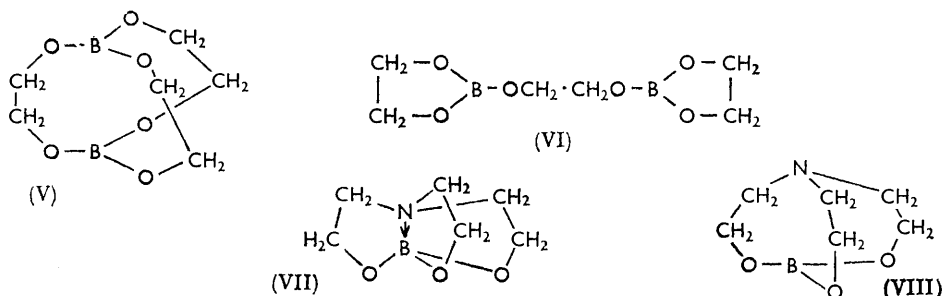
¹⁰ Pictet and Geleznoff, *Chem. Ber.*, 1903, **36**, 2219.

possible to distinguish between the two possible structures (V) and (VI). The infrared spectrum of triethyleneglycol diborate is listed in the Experimental section.

DISCUSSION

In his studies of the structural aspects of organoboron chemistry, H. C. Brown¹¹ proposed the triptych structure (VII) for triethanolamine borate. A possible alternative is the "cage" structure (VIII).

The main objection to the "triptych" structure was that amines do not normally co-ordinate to boron in borate esters, since such co-ordination would require rehybridization of the trigonal boron atom, with subsequent loss of energy from the $p_\pi-p_\pi$ overlap of non-bonding orbitals on the oxygen atoms with the vacant p_π -orbital on the boron atom. However, the reduced donor activity of the lone pair of electrons on the nitrogen atom was considered to favour the "triptych" structure. Further evidence now comes from infrared data: the strongest band in the spectrum occurs at 1090 cm^{-1} and is accompanied by a shoulder at 1103 cm^{-1} ; these are assigned to the $^{11}\text{B-N}$ and $^{10}\text{B-N}$ stretching modes, respectively.



The present work reports the synthesis of azaboratricycloundecane in which no loss of delocalization energy need occur in the formation of a "triptych" structure. The structure (I) is consistent with the physical properties of the compound; its stability towards air, peroxidic oxidizing agents, and electron-donor molecules also indicate that the vacant orbital on the boron atom is involved in co-ordination. Boron-11 nuclear magnetic resonance shows a slightly broadened absorption which may be due to a quadrupole relaxation effect of the nitrogen atom. The proton magnetic resonance results, and infrared spectrum, can best be interpreted on the basis of this structure; they also suggest that each of the three rings is essentially planar.

The proton resonance of a compound of structure (I) might conceivably be extremely complex, since it could be regarded as an $A_6B_6C_6$ system. This would simplify to three independent but identical $A_2B_2C_2$ systems, if interaction between the rings were a second-order effect, and further simplification occurs if the proton-proton coupling constants are small in comparison with the chemical shifts. In the limit this corresponds to an $A_2M_2X_2$ system. The predicted spectrum is then a high-field triplet in which the protons on the methylene group attached to the boron atom are split by the neighbouring CH_2 group, a low field triplet in which the protons on the methylene group attached to the nitrogen atom are split by the same CH_2 group, and a quintuplet between these two triplets, in which the protons on the central methylene group are split by the four protons on the neighbouring NCH_2 and BCH_2 groups, as observed. On this analysis, the mean coupling-constant between the protons on the BCH_2 group and those on the neighbouring CH_2 group (J_B) is 6.93 c./sec. , and the mean coupling-constant between the protons on the NCH_2 group and those on the neighbouring CH_2 group (J_N) is 6.28 c./sec. The average spin-spin splitting of the quintuplet should be intermediate between these; the observed value is 6.41 c./sec.

¹¹ Brown and Fletcher, *J. Amer. Chem. Soc.*, 1951, **73**, 2808.

and the broadening of the quintuplet is due to the fact that J_B is not exactly equal to J_N . Slight asymmetry of the two triplets occurs because the system is not pure $A_2M_2X_2$ but tends slightly towards $A_2B_2C_2$. The high-field triplet is broadened by quadrupole interaction with the ^{11}B -nucleus; this lowers the peak heights but the overall areas of the high-field triplet, the quintuplet, and the low-field triplet approximate to the expected ratio 1 : 1 : 1, the actual values being 1 : 0.95 : 1.01.

The infrared spectrum of azaboratricycloundecane (Table 2) also gives information of structural importance. Thus, the absence of terminal olefinic groups (originally present in the triallylamine) is shown by the absence of a band near 1640 cm.^{-1} characteristic of the C=C stretching frequency,⁸ and the absence of bands at 915, 995, 1420, 1830, 3040, and 3090 cm.^{-1} characteristic of the $=CH_2$ out-of-plane deformations, $=CH_2$ in-plane deformations, and terminal $=CH_2$ stretching frequencies. Nor were there any bands near 2400 cm.^{-1} characteristic of the symmetric or antisymmetric BH vibrations.⁷

From simple group-theoretical considerations, a compound $C_9H_{18}NB$ with the "tritych" structure and planar rings (symmetry C_{3v}) should have 16 vibrations of species A_1 , 11 of species A_2 , and 27 of species E, of which only the A_1 and E modes are infrared-active, leading to 43 possible fundamentals; 35 bands are actually observed between 400 and 4000 cm.^{-1} (Table 2), and all except the seven weakest of these have been assigned.

In the CH stretching frequency range, five of the six bands expected were observed. The band at 2954 cm.^{-1} is assigned to the antisymmetric vibration of the hydrogen atoms on the methylene groups adjacent to the boron atom since this mode occurs at higher wave numbers in substituted diboranes than in simple hydrocarbons.¹² Although the antisymmetric CH_3 stretching frequency occurs at 2962 cm.^{-1} ,⁸ the 2954 cm.^{-1} band found in azaboratricycloundecane cannot be attributed to this, since it is not accompanied by a strong band near 1380 cm.^{-1} characteristic of the C- CH_3 symmetric deformation. The band observed at 2920 cm.^{-1} is assigned to the antisymmetric CH_2 vibration of the methylene groups adjacent to carbon atoms only. This band is relatively broad, and may contain contributions from the antisymmetric CH_2 vibrations of the methylene groups adjacent to the nitrogen atom. The bands at 2879, 2857, and 2819 cm.^{-1} are similarly assigned to the CH_2 symmetric modes of the methylene groups adjacent to the boron atom, to carbon atoms only, and to the nitrogen atom, respectively.

The bands at 1467, 1452, and 1429 cm.^{-1} correspond to CH_2 scissor deformations of the methylene groups adjacent, respectively, to carbon atoms only, to the boron atom, and to the nitrogen atom. The bands at 1348 and 1305 cm.^{-1} and the shoulder at 1355 cm.^{-1} are the CH_2 wagging modes, and the CH_2 twists are well resolved at 1250, 1215, and 1162 cm.^{-1} .

It is more difficult to assign the B-N, B-C, and N-C vibrations for azaboratricycloundecane, since there may well be considerable coupling between these modes. In order to assist in these assignments, the infrared spectrum of triethanolamine borate was re-examined. Weidmann and Zimmerman¹³ studied the spectrum of triethanolamine borate over a limited range, and assigned bands at 900 and 1269 cm.^{-1} to the B-N absorption. The assignment at 900 cm.^{-1} was based on the assignment¹⁴ of a strong band at 918 cm.^{-1} in the spectrum of borazole to the BH-NH in-plane bending mode, but recent work¹⁵ has revealed extensive coupling in the spectrum of borazole, and indicates that ν_{13} , ν_{14} , etc. contain an appreciable proportion of the B-N stretching modes. Similarly, the assignment at 1269 cm.^{-1} in the spectrum of the borate¹³ was based on the assignment¹⁴ of the strong band at 1194 cm.^{-1} in the spectrum of dimethylaminoborane, Me_2NBH_2 , to the B-N vibration. However, it is probable that this compound is dimeric.¹⁶ In the adduct, trimethylborane-ammonia, where the B-N bond approximates more closely to that in the

¹² Lehmann, Wilson, and Shapiro, *J. Chem. Phys.*, 1960, **32**, 1786; 1961, **34**, 476, 783.

¹³ Weidmann and Zimmerman, *Annalen*, 1959, **620**, 4.

¹⁴ Price, Frazer, Robinson, and Longuet-Higgins, *Discuss. Faraday Soc.*, 1950, **9**, 131.

¹⁵ Watanabe, Narisada, Nakagawa, and Kubo, *Spectrochim. Acta*, 1960, **16**, 78.

¹⁶ Wyman, Niedenzu, and Dawson, *J.*, 1962, 4068.

borate, the B-N absorption has been assigned¹⁷ at 1105 cm.⁻¹, and in compounds of the type Me₂BNR₂ where there is extensive coupling with NR₂ vibrations and partial double-bonding, it has been assigned¹⁸ to bands in the region 1447—1525 cm.⁻¹. Taylor¹⁹ also records extensive coupling between B-N and N-C modes in a number of borane adducts, but finds the B-N stretching frequency is in the range 787—667 cm.⁻¹. In the spectrum of triethanolamine borate, the strongest band occurs at 1090 cm.⁻¹ and is assigned to the B-N stretching frequency. It is also relevant that the strong band near 1350 cm.⁻¹ in 3-co-ordinate borate esters due to the antisymmetric B-O stretching frequency⁷ is absent in the spectrum of triethanolamine borate; it is replaced by a strong band at 1064 cm.⁻¹ characteristic of the antisymmetric B-O stretching frequency of 4-co-ordinate boron.

In azaboratricycloundecane, strong bands occur at 1271, 1135, and 1039 cm.⁻¹, and the band at 1135 cm.⁻¹ has an accompanying shoulder at 1144 cm.⁻¹. The B-C antisymmetric stretching frequency occurs near 1125 cm.⁻¹ in a number of trialkylboranes,²⁰ and near 1160 cm.⁻¹ in compounds of the type Me₂BNR₂.¹⁸ The bands at 1135 and 1144 cm.⁻¹ are therefore assigned to the ¹¹B-C₃ and ¹⁰B-C₃ antisymmetric stretching modes, and the band at 1271 cm.⁻¹ to the B-N stretching mode. The N-C stretching frequencies in Me₃NBH₃ have been identified¹⁹ at 850 and 1003 cm.⁻¹, and at 990 and 1111 cm.⁻¹ in Me₂NBMe₂.¹⁸ On the basis of this and previous work,⁸ the band at 1039 cm.⁻¹ in azaboratricycloundecane is assigned to the antisymmetric N-C₃ stretching vibration, and the band at 900 cm.⁻¹ to the N-C₃ symmetric mode. Similarly,¹⁸ the band at 660 cm.⁻¹ in azaboratricycloundecane is assigned to the symmetric B-C₃ stretching vibration.

EXPERIMENTAL

Intermediates and Solvents.—Light petroleum (b. p. 100—120°) was dried over sodium and distilled from lithium aluminium hydride before use. Other solvents were purified by standard procedures. Triethylamine-borane was prepared as previously described.¹ Triallylamine was prepared by the reaction of aqueous ammonia with allyl bromide.²¹ The fraction b. p. 152—156° was used (Found: C, 78.4; H, 10.9; N, 10.3. Calc. for C₉H₁₅N: C, 78.8; H, 10.9; N, 10.2%). Triallylborane was prepared by the reaction of allylmagnesium bromide with boron trifluoride-diethyl ether.²² The fraction b. p. 58—62°/13 mm. was collected.

1-Aza-5-boratricyclo[3,3,3,0]undecane.—A solution of triallylamine (41 g.) in 300 ml. of light petroleum (b. p. 100—120°) was placed in a 1 l. three-necked flask, and a slight excess of dry hydrogen chloride passed in. The hydrochloride separated as an orange oil and a further 11 g. of triallylamine was then added to ensure there was no excess of hydrogen chloride present. The heterogeneous mixture was refluxed with vigorous stirring, and a solution of triethylamine-borane (42 g.) in light petroleum (100 ml.) added slowly under nitrogen, after which the mixture was refluxed for 5 hr. The solid which precipitated (a mixture of polymer and triethylamine hydrochloride) was filtered in a nitrogen-filled glove box, washed several times with small quantities of light petroleum, and the washings added to the filtrate. The bulk of the solvent was then removed by fractionation at normal pressure. The residual viscous liquid was fractionated at reduced pressure, the remaining solvent being collected in a liquid-nitrogen trap which was periodically emptied, care being taken to ensure that no air was admitted to the distillation apparatus. Three volatile fractions were obtained together with a brown residue which was not examined further. In a subsequent preparation under similar conditions it was noticed that appreciable quantities of propylene were also evolved. Fraction 1 (b. p. 30—45°/0.1 mm.) was a colourless liquid (~0.5 ml.) comprising a head fraction of the main product contaminated with the last traces of solvent. Fraction 2 (b. p. 45—50°/0.1 mm.) was a mixture (~10 ml.) of white crystals and a colourless liquid; it solidified in the condenser, which was subsequently warmed so that the product could be collected in one arm of the multiple receiver. This fraction completely solidified on cooling to 0° and was purified by vacuum sublimation or by steam

¹⁷ Goubeau and Becher, *Z. anorg. Chem.*, 1952, **268**, 1.

¹⁸ Becher, *Spectrochim. Acta*, 1963, **19**, 575.

¹⁹ Taylor, Preprints of Papers, Internat. Symposium on Boron-Nitrogen Chemistry, U.S. Army Research Office—Durham, Duke University, Durham, North Carolina, U.S.A., April 1963, p. 198.

²⁰ Lehmann, Wilson, and Shapiro, *J. Chem. Phys.*, 1958, **28**, 777.

²¹ Benjamin and Butler, *J. Chem. Educ.*, 1951, **28**, 191.

²² Topchiev, Paushkin, and Prokhorova, *Doklady Akad. Nauk S.S.S.R.*, 1959, **129**, 598.

distillation to give air-stable crystals of azaboratricycloundecane, m. p. 123°. The infrared spectra of resublimed crystals and crystals purified by steam-distillation were identical. (Found: C, 71.2; H, 12.2; B, 7.15; N, 9.25; $M(\text{vap.})$ 158. $\text{C}_9\text{H}_{18}\text{BN}$ requires C, 71.5; H, 12.0; B, 7.15; N, 9.25%, M , 151). Fraction 3 (b. p. 50°/0.1 mm.) was 2 ml. of a colourless liquid which was extremely sensitive to air; the last traces of the fraction fumed violently and had the characteristic odour of an organoborane. Analysis for boron gave a value of 9.27%; the infrared spectrum showed bands near 2400 cm.^{-1} characteristic of B-H modes.⁸ Steam-distillation of this fraction, which may have contained some $\text{H}_3\text{B}\cdot\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{B}$, yielded pure azaboratricycloundecane. The total yield of azaboratricycloundecane from the three fractions was 10 g. (18%).

Dipropylaminopropylboronic Acid.—The aqueous solution from the steam-distillation of azaboratricycloundecane, yielded white crystals on cooling. After recrystallization from water, these melted at 107° (Found: C, 58.0; H, 11.3; B, 6.0; N, 7.5. $\text{C}_9\text{H}_{22}\text{NBO}_2$ requires C, 57.8; H, 11.8; B, 5.8; N, 7.5%).

Stability of 1-Aza-5-boratricyclo[3,3,3,0]undecane towards Alkaline Potassium Persulphate.—Crude azaboratricycloundecane (0.53 g.) was treated with potassium persulphate (11 g.) and 13% potassium hydroxide solution (25 ml.) in a silica flask fitted with reflux condenser, in an attempt to obtain an analysis for boron. The mixture was refluxed for 2 hr., 5 ml. of 30% hydrogen peroxide was added, and the mixture heated for a further 2 hr. Pure azaboratricycloundecane (0.26 g.) was recovered by steam-distillation.

Hydrolysis of Dipropylaminopropylboronic Acid with Aqueous Potassium Hydroxide.—Dipropylaminopropylboronic acid was refluxed with 2M-potassium hydroxide solution for 24 hr. The product was extracted with ether and identified as tripropylamine by preparation of the picrate, m. p. 115–116° (lit.,²³ 116°). The hydrolysate was acidified, and after addition of mannitol, was titrated for boric acid against barium hydroxide solution, the end-point being determined with a pH meter. Approximately 40% hydrolysis had taken place.

Attempted Dehydration of Dipropylaminopropylboronic Acid.—The methods tried were (a) sublimation under high vacuum, (b) slow sublimation at 100° in dry air at atmospheric pressure, (c) storage in a desiccator over phosphorus pentoxide for 14 days. There was no change in the infrared spectrum after any of these treatments, the O-H band did not decrease in intensity, and no strong band developed at $\sim 1350\text{ cm.}^{-1}$ in the B-O stretching region.⁷

Hydroboration of Triallylborane.—Solutions of triallylborane (32.9 g.) in light petroleum (150 ml.), and triethylamine-borane (30.0 g.) in light petroleum (150 ml.) were added at the same rate (1 drop per second) to 200 ml. of the same solvent and refluxed under nitrogen in standard Quickfit apparatus. The bulk of the solvent and liberated triethylamine were removed at normal pressure, and the remainder under reduced pressure. A colourless, gelatinous material, presumably polymeric, remained in the flask. Strong heating of this gave a number of fractions, and also produced propylene. A non-volatile residue remained. Fractions 1, 2, and 3 were mainly last traces of solvent and triethylamine (gas-liquid chromatography and infrared spectra). Fractions 4, 5, and 6 contained components which were similar to each other (gas-liquid chromatography) with slight variations in quantities of the high- and low-boiling constituents. Fraction 7 was similar to fractions 4, 5, and 6, but contained predominantly the high-boiling constituents of fractions 4–6, and showed B-H bands in the infrared spectrum.

In the separation of fraction 6 by chromatography, the retention time of the major constituent was 6.43 min. compared with 1.19, 2.37, and 4.43 min. for the reference compounds n-heptane, n-octane, and n-nonane [Found: C, 73.9; H, 12.1; B, 15.5%; M , 150 (cryoscopic in cyclohexane). $\text{C}_9\text{H}_{18}\text{B}_2$ requires C, 73.0; H, 12.2; B, 14.7%; M , 148].

Peroxide Hydrolysis of 1,5-Diborabicycloundecane.—Diborabicycloundecane (1.52 g.) was placed in a 250-ml. two-necked flask, and ethyl alcohol (15 ml.) was added. A vigorous evolution of gas was observed. Potassium hydroxide (3.5 g.) was added, followed by 15 ml. of 100-vol. hydrogen peroxide solution, and the mixture refluxed for 2 hr. The organic fraction was extracted with ether, and the ethereal extract evaporated under reduced pressure. Distillation of the remaining oil yielded about 0.3 ml. of colourless viscous liquid (Found: C, 49.8; H, 10.8%. Calc. for $\text{C}_5\text{H}_8\text{O}_2$: C, 47.3; H, 10.5%). Infrared examination confirmed that the product was 1,3-propanediol.

Triethanolamine Borate.^{9,11}—Triethanolamine was purified by low-pressure distillation. The fraction distilling at 140° at oil-pump vacuum was used. Triethanolamine (41.7 g.) and boric acid (17.2 g.) were mixed intimately and dehydrated slowly on a vacuum line. Water (14.8 g.,

²³ Cheronis and Entrikin, "Semimicro Qualitative Organic Analysis," Crowell, New York, 1947, 410.

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theory 15.1 g.) was evolved, and the product was purified by vacuum-sublimation at 200° followed by recrystallization from dry pyridine, m. p. 234.5—235.5° (lit.,^{11,24} 236.5°, 231°). Yield before recrystallization, 43 g., 98%.

Trisethyleneglycol Diborate.—Boric acid (11.5 g.) recrystallized from water was finely ground and mixed with ethylene glycol (17 g.). The flask was slowly evacuated and the water evolved (9.5 g., theory 10.0 g.) was collected in a trap at -196°. After 4 hr. at room temperature the flask was warmed to 50° and maintained there overnight. The product was purified by vacuum-sublimation, followed by recrystallization from dioxan-ether and carbon tetrachloride, and finally by a further vacuum-sublimation (Found: C, 35.7. C₆H₁₂O₆B₂ requires C, 35.8%). It was noticed that the compound formed a gel on crystallization from carbon tetrachloride, from which residual solvent was removed on evacuation.

Determination of Molecular Weight.—The Rast determinations were made by standard microanalytical procedure. Vapour densities of volatile compounds were determined by standard procedure in a calibrated bulb which could be attached to the vacuum line. For thermally stable, less volatile compounds a specially designed apparatus was used.

Vapour-pressure Measurements.—The apparatus mentioned above was used with larger samples to prevent complete volatilization.

Infrared Spectra.—Routine spectra for identification purposes were obtained on a Perkin-Elmer "Infracord" model R Spectrophotometer (650—4000 cm.⁻¹). Definitive spectra were recorded over the range 375—8000 cm.⁻¹ on a calibrated Unicam S.P. 100 spectrometer. The infrared spectrum of azaboratricycloundecane (Table 2) was obtained in carbon tetrachloride and carbon disulphide solutions.

For triethanolamine borate, the infrared spectrum was recorded from a pressed potassium-bromide disc, and the frequencies (cm.⁻¹) and, in parentheses, relative intensities (ϵ) were: 432 (36), 517 (31), 563 (20), 623 (27), 738 (74), 900 (87), 913 (66), 928 (37), 937 (47), 1008 (79), 1034 (74), 1042 (62), 1064 (95), 1090 (100), 1103 (95), 1125 (79), 1169 (63), 1226 (23), 1237 (28), 1269 (65), 1337 (27), 1349 (36), 1357 (30), 1377 (57), 1456 (25), 1461 (27), 1473 (42), 1489 (39), 1509 (16), 2701 (8.7), 2725 (6.3), 2863 (51), 2904 (18), 2953 (17), 2972 (21), 2990 (25), 3013 (17).

A solution of trisethyleneglycol diborate in carbon tetrachloride had absorption bands at 671 (20), 690 (7), 919 (8), 932 (10), 950 (9), 1028 (16), 1048 (26), 1066 (11), 1080 (10), 1110 (12), 1120 (11), 1232 (27), 1248 (14), 1296 (7), 1332 (16), 1358 (28), 1406 (36), 1424 (24), 1444 (67), 1480 (37), 1504 (47), 1532 (20), 2910 (9), 2975 (9).

Nuclear Magnetic Resonance Spectra.—Proton spectra were obtained on a Varian Associates A60 spectrometer and an A.E.I. RS2 Spectrometer at 60 Mc./sec. The quoted values of the coupling-constants and chemical shifts were obtained on the latter instrument by the side-band technique, and were mean values of several upfield and downfield sweeps. Boron-11 spectra were obtained on a Varian Associates V-4300 spectrometer at 15.1 Mc./sec. and on the A.E.I. model RS2 spectrometer at 20 Mc./sec.

Analyses.—Where possible, analyses were obtained by conventional microanalytical procedures. However, owing to the stability of a number of compounds, analysis for boron was carried out by the following procedure. Fuming nitric acid, s.g. 1.5 (10 ml.) was placed in a heavy-walled Pyrex tube, 40 × 2 cm., sealed at one end and was frozen in liquid nitrogen. The compound (0.3—0.5 g.) was weighed out in a stoppered silica weighing-tube which was opened just before it was placed in the reaction tube. The tube was sealed, placed in a steel guard-tube, and allowed to warm to room temperature, the tube being gently agitated to ensure contact of the reactants. (With certain compounds serious explosions sometimes resulted, shattering the glass tube.) The tube was then heated in a furnace for at least 18 hr. at 180—200° to ensure complete oxidation. The tube was cooled and opened, and the contents were transferred to a beaker and diluted with water. Carbon dioxide was boiled off for 10 min., and the solution was cooled and made up to 250 ml. Aliquot portions were titrated potentiometrically against standard barium hydroxide solution to the strong-acid end-point at pH 6.3. Preliminary addition of several drops of strong alkali reduced the need for large volumes of barium hydroxide. The solution was then saturated with mannitol, and titrated to the mannitol-boric acid end point (pH 8.0). A blank determination on the reagents was subtracted from the titre. It was found essential to use very large concentrations of mannitol in order to obtain a sharp end-point. Analysis for carbon was carried out by the method of Dunstan and Griffiths,²⁵

²⁴ Hein and Burkhardt, *Z. anorg. Chem.*, 1952, **268**, 159.

²⁵ Dunstan and Griffiths, *Analyt. Chem.*, 1961, **33**, 1598.

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the apparatus being modified to deal with volatile compounds by the inclusion of a bulb-breaking device in the oxidation apparatus.

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