

Studies on the Chemistry of Aziridine Boranes

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1. Borane addition compounds have been prepared from the following aziridines: aziridine, *N*-(2-aminoethyl) aziridine, *N*-(2-hydroxyethyl) aziridine and *N*-(2-cyanoethyl) aziridine. The methods used for the preparation of aziridine boranes are useful also for the preparation of alkylamine boranes.

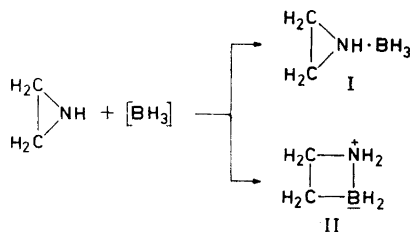
2. The dipole moment of aziridine borane has been determined to be 4.45 ± 0.01 D.

3. The reactivity of the compounds with halogens, hydrohalogenic acids, quinone, benzaldehyde, and a number of other substances has been investigated. It appears likely that the reaction with halogens, hydrohalogenic acids, and oxonium ions is initiated by an attack on the aziridine ring rather than on the BH_3 group.

4. *N*-(Triethylene) cyclotriborazane has been prepared.

The strongly reducing properties of alkylamine boranes make these compounds interesting as potential radical scavengers and radioprotective agents. Certain compounds of this category have therefore been synthesized and investigated in this laboratory. During these studies it was found that the reaction product between aziridine (and derivatives) and borane showed an unexpected chemical reactivity which warranted a closer study of the structure and chemistry of these compounds. The studies also led to simplified methods for the preparation of certain alkylamine boranes and aziridine boranes.

The reaction between aziridine and borane could conceivably lead to the following substances:



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or possibly to a polymer of the type $(\text{NH}_2\text{CH}_2\text{CH}_2\text{BH}_2)_n$.

Burg and Good¹ isolated a substance, m.p. about 40° , from the reaction between diborane and aziridine, to which structure I was tentatively assigned. A product prepared by our method from sodium borohydride and aziridine (m.p. $47-48^\circ$) was initially assigned the structure II in a preliminary communication,² since at the time this structure appeared plausible from NMR, IR, and reactivity data of the compound.

Conclusive evidence for structure I for the compound prepared by us was finally obtained by ^{11}B NMR analysis performed by Williams,³ and by crystal structure determination by Ringertz.⁴

The present article will chiefly describe preparative methods and some chemical properties of aziridine boranes.

PREPARATION OF AZIRIDINE BORANES

A convenient method for the preparation of alkylamine boranes consists of reacting an alkylammonium halide with lithium borohydride⁵ or with sodium borohydride.⁶ However, in the case of aziridine and derivatives the ammonium salts are not very stable and not easily accessible. Therefore direct application of the above methods is not feasible. For the liberation of borane from sodium borohydride in the presence of aziridine the following two methods have been used: (a) thermal decomposition in water-tetrahydrofuran; and (b) decomposition by glacial acetic acid in anhydrous tetrahydrofuran.

With method (a) it was found that the water concentration was of profound importance for the product yield (*cf.* Fig. 1). Thus optimum yield was obtained at about 25% (3 ml in Fig. 1) water concentration. This may be explained in the following way. Too little water prevents complete dissolving of sodium borohydride and too much water makes the mixture a poor solvent for borane and/or prevents its association with aziridine. From the reaction mixture white needles could be isolated with the elemental composition $\text{C}_2\text{H}_8\text{BN}$. Mass spectrographic analysis performed at 25° gave a molecular weight corresponding to one unit of the above formula.

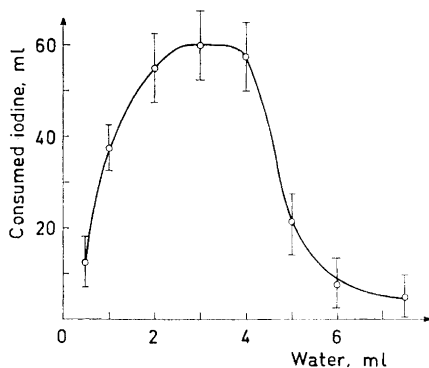


Fig. 1. Effect of water concentration on the yield of aziridine borane. The yield is proportional to amount of iodine consumed. For details, see Experimental Section, paragraph 13.

For the preparation of *N*-substituted aziridine boranes and alkylamine boranes the preferred method is to decompose sodium borohydride by acetic acid in the presence of an *N*-substituted aziridine. A good solvent for this reaction is tetrahydrofuran.

STRUCTURAL INVESTIGATIONS

The structures of the prepared derivatives of aziridine borane was mainly investigated by NMR analysis. From the chemical shifts of the ring methylene protons (Table 1) it has been concluded that these compounds contained the aziridine ring and thus were true derivatives of aziridine borane. For a detailed investigation and discussion of one of the derivatives, see Ref. 3.

DIPOLE MOMENT OF AZIRIDINE BORANE

Nöth and Beyer ⁷ and Weaver and Parry ⁸ have determined the dipole moments of a number of alkylamine boranes in solution. As expected for these very polar compounds the dipole moments are high, 4.5–5 D. (Table 2). Nöth and Beyer ⁷ have shown that vectorial addition of the bond moment of the N—BH₃ group (3.90 D) to the dipole moment of alkylamines gives to a

Table 1. Methylene group signals from NMR spectra. [CH₂]₂N=aziridine ring.

	Ring CH ₂ τ ppm	Solvent
[CH ₂] ₂ NH	8.4	CDCl ₃
[CH ₂] ₂ NHBH ₃	8.1	CDCl ₃
	7.65	
[CH ₂] ₂ NHBH ₃	8.55	DMSO- <i>d</i>
	7.9	
[CH ₂] ₄ NCH ₂ CH ₂ NH ₂	9.1	DMSO- <i>d</i>
	8.6	
[CH ₂] ₂ NCH ₂ CH ₂ NH ₂ BH ₃	7.95	DMSO- <i>d</i>
	7.8	
 BH ₃		
[CH ₂] ₂ NCH ₂ CH ₂ OH	9.1	DMSO- <i>d</i>
	8.6	
[CH ₂] ₂ NCH ₂ CH ₂ OH	8.0	DMSO- <i>d</i>
	7.8	
 BH ₃		
[CH ₂] ₂ NCH ₂ CH ₂ CN	9.0	DMSO- <i>d</i>
	8.5	
[CH ₂] ₂ NCH ₂ CH ₂ CN	8.75	CDCl ₃
	8.2	
[CH ₂] ₄ NCH ₂ CH ₂ CN	7.7	CDCl ₃
	7.6	
 BH ₃		

Table 2. Dipole moments of amine boranes.

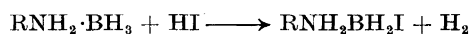
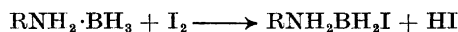
	Dipole moment Debye units	
$\text{NH}_3 \cdot \text{BH}_3$	5.05 ⁸	
$\text{CH}_3\text{NH} \cdot \text{BH}_3$	5.19 ⁷	5.15 ⁸
$(\text{CH}_3)_2\text{NH} \cdot \text{BH}_3$	4.87 ⁷	4.99 ⁸
$(\text{CH}_3)_3\text{N} \cdot \text{BH}_3$	4.45 ⁴	4.69 ⁸
$[\text{CH}_2]_2\text{NH} \cdot \text{BH}_3$	4.45 ± 0.01	

The dipole moments obtained by Nöth and Beyer ⁷ were determined in benzene solutions, whereas Weaver and Parry ⁸ used dioxane. The moment of aziridine borane was determined in benzene.

fair approximation the total dipole moment of several alkylamine boranes. This is not the case with aziridine borane. Using the dipole moment of aziridine (1.89 D ⁸) the value would be around 5.3 D, whereas that found is 4.45 ± 0.01 D. An explanation is probably the inversion of the NH bond in aziridine. The dipole moment is therefore not applicable to aziridine borane, where the configuration is fixed.

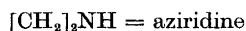
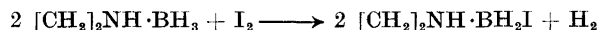
STUDIES ON THE REACTIVITY OF AZIRIDINE BORANES

Reactions with iodine and bromine. Nöth and Beyer ¹⁰ have shown that alkylamine boranes react with iodine with the formation of alkylamine monoiodoboranes:



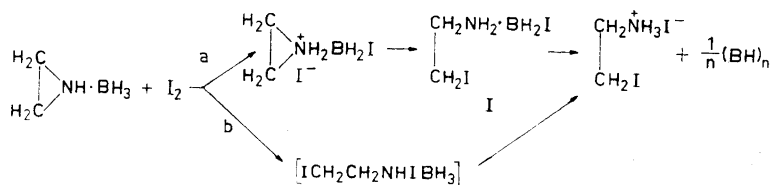
In the presence of excess iodine, no further reaction occurs in benzene. On the other hand Hawthorne ¹¹ has shown that pyridinium phenylborane consumes one mole of iodine per B—H bond in pyridine.

According to the results of Nöth and Beyer ¹⁰ an addition compound between aziridine and borane could be expected to react in the following way with iodine:



However, when aziridine borane reacted with one mole of iodine in CHCl_3 at room temperature, 2-iodoethylammonium iodide precipitated almost immediately in high yield. Bromine was found to react in the same way.

This reaction could be initiated by two different steps: (a) an initial reaction between I_2 and BH_3 , or (b) nucleophilic attack by I_2 on one carbon in the aziridine ring:



In the two possible schemes outlined above the intermediate (I) would be expected to be a relatively stable one. In fact Nöth and Beyer¹⁰ have isolated a number of compounds of a similar structure and these authors found no evidence for a spontaneous reaction as outlined in (a). This leaves the lower reaction sequence as the more likely one.

In methanol and chloroform, aziridine itself does not react with iodine at 22° (Table 3). The reactions discussed above thus clearly demonstrate the inductive activation of the aziridine ring by the strongly electrophilic boron atom.

The reactivity of aziridine boranes with iodine has been studied in two solvents and compared to the reactivity of *N*-alkylamine boranes, such as ethylenediamine diborane, triethylamine borane, and diethylamine borane. As can be seen from Table 3 the solvent in which the reaction is carried out

Table 3. Reactivity of alkyl- and aziridine boranes with iodine at 22°. $[CH_2]_2N$ = aziridine ring.

Compound	Equivalents of iodine consumed per mole of compound in	
	CH_3OH	$CHCl_3$
$[CH_2]_2NH$	0	0
$[CH_2]_2NCH_2CH_2R$ (R = NH_2 , OH, CN)	0	0
$[CH_2]_2NH \cdot BH_3$	6	4
$[CH_2]_2N \cdot CH_2CH_2NH_2 \cdot BH_3$	10	6
BH_3		
$[CH_2]_2NCH_2CH_2OH$	6	— ^a
BH_3		
$[CH_2]_2NCH_2CH_2CN$	—	4
BH_3		
$(CH_3CH_2)_3NBH_3$	4	—
$BH_3NH_2CH_2CH_2NH_2BH_3$	8–9	4
$(CH_3CH_2)_2NH \cdot BH_3$	4	—

^a The compound is insoluble in $CHCl_3$.

has a profound influence on the amount of iodine consumed. Since it was shown that the initial reaction product from aziridine borane is 2-aminoethyl-iodide, the different amounts of iodine which react, should be due to different degrees of iodination of borane, probably caused by the difference in polarity of the solvents. This conclusion is further augmented by the observation that when this reaction is carried out in a less polar solvent than CHCl_3 , such as benzene, only about 2 equivalents of iodine are consumed per mole of compound.

The *N*-substituted aziridine boranes prepared in this work were all found to give *N*-substituted 2-haloethylamines when reacted with iodine or bromine. Per mole the *N*-substituted aziridine boranes always consumed two equivalents more than the corresponding *N*-alkyl boranes (Table 3). These two equivalents of halogen are obviously used to open the aziridine ring according to the above equation.

Reaction with acids and bases. In water at pH 7 aziridine borane forms a relatively stable solution. In alkaline solution the substance is surprisingly stable as demonstrated by the fact that 50 % of it remains unchanged after 3.5 h of refluxing in 1 M sodium hydroxide (Table 4).

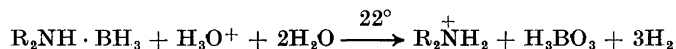
Table 4. Reactivity of aziridine borane.

Aziridine borane reacted with	Reaction medium	Reaction time, h	Temp. °C	Reaction product (% yield)
HCl, 3 M	H_2O	0.1	20°	$\text{H}_3\text{BO}_3 + \text{ClCH}_2\text{CH}_2\text{NH}_2$ (ca. 100 %)
NaOH, 1 M	H_2O	3.5	reflux	$\text{HOCH}_2\text{CH}_2\text{NH}_2$ (ca. 50 %) ^a
Na_3SPO_3	H_2O , pH 10	24	20°	$\text{NH}_2\text{CH}_2\text{CH}_2\text{SPO}_3\text{Na}_2$ (ca. 20 %) ^a
$(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_2$	H_2O , pH 7	1	20°	$\text{HSCH}_2\text{CH}_2\text{NH}_2$ (traces) ^a
$(\text{C}_2\text{H}_5)_3\text{N}$	$(\text{C}_2\text{H}_5)_3\text{N}$	3	reflux	$(\text{C}_2\text{H}_5)_3\text{NBH}_3$ (40 %)
quinone	$(\text{C}_2\text{H}_5)_2\text{O}$	24	20°	quinhydrone (90 %)
$\text{C}_6\text{H}_5\text{CHO}$	C_6H_6	0.5	reflux	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (45 %)
$\text{CH}_2=\text{C}-\text{COOCH}_3$ CH_3	$\text{C}_2\text{H}_5\text{OH}$	24	reflux	no reaction ^a
$\text{C}_6\text{H}_5\text{NO}_2$	C_6H_6	24	reflux	no reaction ^a
$\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$	tetrahydrofuran	1	reflux	no reaction ^a

^a As determined by TLC analysis and spot tests.

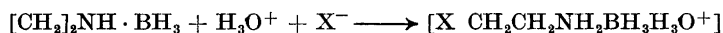
In acid solution, on the other hand, aziridine borane is immediately decomposed with gas evolution. It was shown by mannitol titration that the boron atom of the compound is quantitatively hydrolyzed to boric acid by treatment with aqueous hydrobromic or hydrochloric acids. To investigate the other products, the reaction mixture was treated with 2,4-dinitrofluorobenzene, yielding DNP derivatives. TLC analysis showed the presence of only one derivative, identical in position with the DNP-derivatives of 2-bromoethylamine and 2-chloroethylamine, respectively. No trace of DNP-2-aminoethanol or DNP-polyethylene imine could be detected in the reaction mixtures. The DNP-derivatives were isolated and full identity with the DNP-derivatives of 2-chloro- and 2-bromoethylamine, respectively, was established by IR and NMR spectra and elementary analysis.

The initial step in the degradation of aziridine borane by aqueous hydrohalogenic acids is probably not the result of the reaction with oxonium ions alone which occurs with certain amine boranes:¹¹



Since 2-haloethylamine was isolated the aziridinium ion formed would have then to react with excess hydrohalogenic acids. However, this reaction does not occur easily. It is well known that the aziridinium ion polymerises under these conditions and only trace amounts of 2-haloethylamine is formed. These results have been confirmed during this investigation by coupling the reaction products to 2,4-dinitrofluorobenzene, followed by TLC analysis. The addition of hydrohalogenic acid to the aziridine ring must therefore take place while the N—B bond is still in existence.

On the other hand, oxonium ions as such also react with aziridine borane. This was shown in experiments when Dowex 50 (H⁺) was added to aqueous solutions of the compound. The reaction products were boric acid and 2-aminoethanol. In this case also the aziridine ring seems to have been opened when the N—B bond was still intact.



(X = Cl, Br, or OH)

(Probable transition state complexes for the reaction between borohydrides and oxonium ions have been discussed elsewhere¹²).

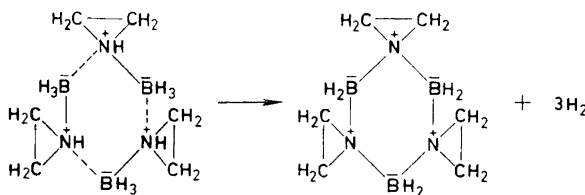
Miscellaneous reactions. Aziridine borane is freely soluble in benzene and in a number of other polar solvents. This is of special interest, since it might be possible to carry out reductions with the compound in lipophilic solvents.

Nöth and Beyer¹³ have shown that alkylamine boranes are able to reduce aldehydes, ketones and acid chlorides, but not esters, acids, or nitro groups.

Our preliminary investigations on the reactivity of aziridine borane seem to indicate that this compound has reducing properties similar to ordinary

amine borane addition compounds (Table 4). In addition, transboranation has been demonstrated to occur between triethylamine and aziridine borane.

Formation of N-(triethylene) cyclotriborazane from aziridine borane. Refluxing a solution of aziridine borane in benzene (but not in strongly polar solvents like alcohols or ethyl acetate) resulted in the formation of a reducing, boron containing substance with a molecular weight corresponding to a trimer of aziridine borane less six hydrogens. It is known that cyclotriborazanes can be formed by heating alkylamine boranes.¹⁴ It therefore appeared likely that the following reaction had taken place:



According to the above scheme strongly polar solvents would be expected to prevent the association between aziridine borane molecules and thus prevent the formation of product. On the other hand, association of amine boranes, especially in benzene solution, is a well known phenomenon.⁶

¹¹B NMR studies on the compound (see Ref. 3) have fully verified the structure of the isolated product as *N*-(triethylene) cyclotriborazane.

EXPERIMENTAL

1. *Aziridine borane. Method a.* 0.8 g (20 mmoles) of NaBH₄, 3 ml of water, 5 ml of tetrahydrofuran, and 0.5 ml (10 mmoles) of aziridine were refluxed for 40 min, whereafter the reaction mixture was extracted with 50 ml of ether. The ether phase was separated, dried (Na₂SO₄), and evaporated. The crystalline substance obtained was dissolved in 5 ml of benzene. After filtration, cyclohexane was carefully added until small crystals or droplets were formed. Just enough benzene to obtain a clear solution was then added. Refrigeration (+2°) gave 0.4 g (70 %) of needle shaped crystals, m.p. 47–48°.

Method b. See Ref. 2. This method can be scaled up 10 times without decrease in the yield (73 %). (Found: C 42.0; H 14.3; N 24.8; B 19.0. Calc. for C₂H₈BN (mol. wt. 57) C 42.2; H 14.2; N 24.6; B 19.0). Mol. wt. (mass spectral at 25°): 57.

2. *Alkylamine boranes* like triethylamine borane, diethylamine borane, and ethylendiamine diborane have been prepared by method 1 b in yields up to 85 %.

3. *Addition compound between borane and N-(2-aminoethyl)-aziridine borane.* 9.2 ml (160 mmoles) of acetic acid dissolved in 100 ml of tetrahydrofuran were added with rapid stirring during 2 h to a mixture of 6.4 g (166 mmoles) of NaBH₄ and 6.6 g (84 mmoles) of *N*-(2-aminoethyl) aziridine in 100 ml of tetrahydrofuran. The temperature was maintained at 18–22°. When the gas evolution has stopped, the mixture was filtered and evaporated to dryness. After recrystallisation from water the substance melted at 105–106°. Yield 5.7 g (60 %). (Found: C 42.3; H 15.0; N 24.2; B 18.0. Calc. for C₄H₁₇N₂B₂ (mol. wt. 114.8) C 41.9; H 14.9; N 24.5; B 18.8). Mol. wt. (mass spectral at 25°): 114.

4. *N-(2-Hydroxyethyl) aziridine borane.* 5.75 ml (100 mmoles) of acetic acid dissolved in 65 ml of tetrahydrofuran were added with rapid stirring during 3 h to a mixture of 4.0 g (105 mmoles) of NaBH₄ and 6.6 g (76 mmoles) of *N*-(2-hydroxyethyl) aziridine in 100 ml of carefully purified tetrahydrofuran. When gas evolution had ceased the mixture was worked up as in 3. The dry material was redissolved in 50 ml of tetrahydrofuran, filtered, and reprecipitated by the addition of cyclohexane. This preparation was chro-

matographically pure (TLC). Yield 5.8 g (76 %). (Found: C 47.0; H 11.8; N 13.5; B 10.6. Calc. for C_4H_9NOB (mol. wt. 101.0) C 47.5; H 12.0; N 13.9; B 10.7). Mol. wt. (mass spectral at 25°): 101.

5. *N*-(2-Cyanoethyl)-aziridine borane. The reaction was carried out as in 4 using 4.6 ml (80 mmoles) of acetic acid in 50 ml of tetrahydrofuran and 7.6 g (80 mmoles) of *N*-(2-cyanoethyl) aziridine, 3.2 g (84 mmole) of $NaBH_4$ in 100 ml of tetrahydrofuran. Yield 8.5 (94 %) of an oily product, which was purified by TLC on silica gel (solvent, 5 % methanol in chloroform). The fastest moving spot, which was the largest one and contained about 90 % of the material, was eluted with benzene and evaporated. (Found: C 55.3; H 10.3; N 24.9; B 9.7. Calc. for $C_6H_{11}N_2B$ (mol. wt. 110.0): 54.6; H 10.1; N 25.5; B 8.84). Mol. wt. (mass spectral at 25°): 110.

6. *The reaction between aziridine borane and iodine or bromine.* The reactions were carried out at 20° by mixing a solution of the aziridine boranes (2 mmoles) in chloroform (50 ml) with 2 equivalents of halogen (in case of the *N*-(2-aminoethyl) derivative 6 equivalents). The reaction products precipitated almost immediately.

Aziridine borane and iodine gave 87 % yield of $ICH_2CH_2NH_3^+I^-$ m.p. 189–191° (from nitromethane). (Ref. 15, m.p. 192–194°). (Found: C 8.2; H 2.4; N 4.8; I 84.3. Calc. for $C_2H_7NI_2$: C 8.0; H 2.4; N 4.7; I 85.0). NMR in DMSO-*d*: $\tau=6.8$ ppm (4 H,S), $\tau=2.2$ (3 H,S).

Aziridine borane and bromine gave 89 % yield of $BrCH_2CH_2NH_3^+Br^-$ m.p. 176–177° (from nitromethane) undepressed by admixture with an authentic sample. NMR in DMSO-*d*: $\tau=6.8$ ppm (2 H,t) $\tau=6.4$ ppm (2 H,t) and $\tau=1.9$ ppm (3 H,S).

N-(2-Aminoethyl) aziridine diborane and iodine gave 85 % yield of the labile compound $[ICH_2CH_2NH_2CH_2CH_2NH_3^+, 2I^-] BH_2I$, m.p. 120–122°. This substance reduced silver ions, and IR spectra showed the presence of BH-absorptions at 1168 cm^{-1} and 2350 cm^{-1} . After recrystallisation from isopropanol it melted at 156–158° and consisted of $ICH_2CH_2NH_2CH_2CH_2NH_3^+, 2I^-$. (Found: C 10.4; H 3.0; N₂ 5.87; I 79.8. Calc. for $C_4H_{13}N_2I_3$: C 10.2; H 2.8; N 5.95; I 81.0).

Similar treatment of *N*-(2-aminoethyl)-aziridine diborane with slight excess of bromine in chloroform gave 90 % of $BrCH_2CH_2NH_2CH_2CH_2NH_3^+, 2Br^-$, m.p. 175–177° (from methanol-chloroform) (Ref. 16, 172°). (Found: C 14.4; H 4.2; N 8.5; Br 71.5. Calc. for $C_4H_{13}N_2Br_3$: C 14.6; H 4.0; N 8.5; Br 72.6).

N-(2-Cyanoethyl)-aziridine borane and iodine gave about 85 % yield of $ICH_2CH_2NH_2CH_2CH_2CN, I^-$, m.p. 122–124° (from isopropanol). (Found: C 16.4; H 2.8; N 7.6; I 72.9. Calc. for $C_6H_{10}N_2I_2$ (mol. wt. 352.0): C 17.1; H 2.9; N 8.0. I 72.0). Mol. wt. (mass spectral at 25°): 223 (352-HI-H).

N-(2-Hydroxyethyl)-aziridine borane and iodine gave 73 % yield of $HOCH_2CH_2NH_2CH_2CH_2I, I^-$, m.p. 122–124°. (Found: C 14.4; H 3.3; N 4.3; I 75.0. Calc. for $C_4H_{11}NOI_2$: 14.0; H 3.2; N 4.1; I 74.0).

7. *The reaction between aziridine borane and hydrohalogenic acids.* 0.5 g of aziridine borane were treated with 15 ml of 5 M HBr or HCl. When gas evolution had ceased the mixture was evaporated to dryness. Aliquots of the solid residue were taken out, weighed, and boric acid was determined titrimetrically in the presence of mannitol. The yield of boric acid varied between 96 and 99 % of the theoretical amount.

The DNP-derivatives were prepared by dissolving the solid residue in 80 % ethanol (10 ml) and making the solution basic with triethylamine. 50 % excess of 2,4-dinitrofluorobenzene was added. After 30 min the mixture was evaporated to dryness and recrystallized from water-ethanol. (Found: C 33.1; H 2.84; N 14.7; Br 27.8. Calc. for $C_8H_9N_3O_4Br$ (m.p. 91–93°): C 33.1; H 2.78; N 14.5; Br 27.6). (Found: 39.3; H 3.26; N 17.4; Cl 14.7. Calc. for $C_8H_9N_3O_4Cl$ (m.p. 87–93°): C 39.1; H 3.29; N 17.1; Cl 14.4).

8. *The reaction between benzaldehyde and aziridine borane.* 2.3 g of benzaldehyde and 0.5 g of aziridine borane were dissolved in 100 ml benzene. After refluxing for 30 min 25 ml of 2.5 M sulphuric acid were added under rapid stirring. The benzene phase was separated, dried (Na_2SO_4), and evaporated. Distillation gave 1.0 g of pure benzyl alcohol, b.p. 110–115° at 25–30 Torr, identified by TLC and NMR.

9. *The reaction between quinone and aziridine borane.* 2.85 g of quinone and 0.5 g of aziridine borane were dissolved in 85 ml of ether. The precipitate was collected after 24 h and washed with ether. 2.5 g of quinhydrone were thus obtained, identified by TLC, mixed melting point, and mass spectrum.

10. *The reaction between triethylamine and aziridine borane.* 300 mg of aziridine borane were refluxed for 4 h in 30 ml of triethylamine. After evaporation the substance was chromatographed on a silica gel column with chloroform as the eluent. 250 mg of triethylamine borane, giving identical NMR and IR spectra with an authentic sample, were thus obtained.

11. *N-(Triethylene) cyclotriborazane.* 1 g of aziridine borane was refluxed for 4 h in about 30 ml of benzene. After evaporation to dryness and recrystallisation (ethanol) 0.7 g of a white crystalline substance were obtained (subl. 150–160°, 760 Torr). (Found: C 44.2; H 11.3; B 18.8; N 25.8. Calc. for $C_6H_{18}B_3N_3$ (mol. wt. 164.68): C: 43.8; H 11.0; B 19.7; N 25.6). Mol. wt. (mass spectral at 25°): 164.

12. *Dipole moment measurements* were carried out using a dipolmeter Type DM 0.1, Wissenschaftlich-Technischen Werkstätten, GmbH, Weilheim, Obb., Germany. The following values were obtained in benzene:

w_2	$\Delta\epsilon_{12}$	Δn^2	Dipole moment D
0.01359	0.510	-0.0021	4.44
0.01751	0.661	-0.0033	
0.00490	0.213	-0.0003	4.45
0.0111	0.392	-0.0009	

where w_2 is mole fraction of aziridine borane, $\Delta\epsilon_{12}$ is difference in dielectric constant, Δn^2 difference in squares of refractive indexes. The method of calculation was that of Hedestrand.¹⁷

13. *Investigation of the effect of water concentration on the yield of aziridine borane.* 0.8 g of $NaBH_4$, (8-x) ml of water, x ml of tetrahydrofuran and 0.5 ml of aziridine were refluxed for 40 min. After cooling 1.00 g of the upper phase was treated with about 15 ml of water and 5 ml of glacial acetic to decompose remaining $NaBH_4$. The mixture was immediately titrated to persistent colour with iodine (50 equiv./ml) in methanol.

14. *Instrumentation and chemicals.* IR spectra were recorded on a Perkin Elmer Model 225 instrument. For the NMR spectra a Varian Model A60A high resolution instrument was used. The mass spectrometer used was an LKB 9000 instrument. TLC was carried out on Silica gel HF 254 (Merck) in methanol-chloroform, 1:20, and ethylacetate-propanol- H_3N , 45:35:20.

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