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THE REACTION OF AZIRIDINE WITH SODIUM BOROHYDRIDE

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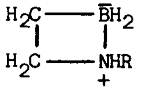
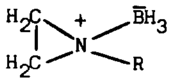
The reaction between aziridine and sodium borohydride was reported by Akerfeldt and Hellstrom (1) to give the four-membered heterocyclic compound (Ia) rather than aziridine-borane (IIa). This reaction was of interest to us in connection with some other work. We



Ia R = H

b R = CH_3



IIa R = H

b R = CH_3

considered that the evidence presented by Akerfeldt and Hellstrom in favour of the proposed structure Ia was inconclusive since it was based on one of several possible interpretations of an NMR spectrum. We, therefore, repeated the reaction of aziridine with sodium borohydride in aqueous tetrahydrofuran according to the reported procedure (1).

A product was isolated which had the same physical properties as those reported by Akerfeldt and Hellstrom and which after purification by vacuum sublimation analysed as C_2H_8BN (Found: C, 42.4; H, 14.0; B, 18.9; N, 24.6. Calc. for C_2H_8BN: C, 42.2; H, 14.2; B, 19.0; N, 24.6%). The infrared spectrum of this compound showed the presence of $\overset{+}{N}$-H (3300 and 2740 cm^{-1}) as would be expected for either Ia or IIa.

On the other hand, in the case of Ib and IIb, where R = CH_3, only Ib contains an $\overset{+}{N}$-H group. We, therefore, carried out the reaction under the same conditions with N-methylaziridine as the donor molecule and isolated a white solid (42%) which after vacuum sublimation melted at 57-58° and analysed as $C_3H_{10}BN$. (Found: C, 51.1; H, 13.8; B, 15.3; N, 19.8. Calc. for $C_3H_{10}BN$: C, 50.8; H, 14.2; B, 15.2; N, 19.8%). The infrared spectrum of this product showed no absorptions characteristic of an N-H group, which eliminates Ib as a possible structure and suggests that the compound is IIb. By analogy the compound obtained by Akerfeldt and Hellstrom would thus be IIa.

The ^{11}B NMR spectra of the compounds C_2H_8BN and $C_3H_{10}BN$, from aziridine and N-methylaziridine respectively, provided convincing evidence for the structures IIa and IIb. The presence of a BH_3 group in both compounds was evident from the presence of a symmetrical 1:3:3:1 quartet in the spectrum of each. The coupling constants J_{BH} of 91 and 96 cps are in agreement with the values reported for other amine-boranes (2) thus providing additional evidence for structures IIa and IIb. The ^1H NMR spectrum of the compound C_2H_8BN showed an A_2B_2 pattern due to the methylene hydrogens. This is consistent with the structure IIa, since the methylene hydrogens <u>cis</u> and <u>trans</u> to the BH_3 group are not magnetically equivalent and spin-spin coupling gives rise to the observed pattern. The NMR spectra of aziridine and various N-substituted aziridines have been reported to show an A_2B_2 pattern for the dimethylene moiety when the rate constant for the nitrogen inversion process is small compared with the chemical shift, ν_{AB} (3,4). In compound IIa an A_2B_2 pattern would be expected since there is no opportunity for nitrogen inversion. The ^{11}B and ^1H NMR data are summarized in the Table.

Burg and Good (5) obtained a product (m.p. about 40°) from the reaction of aziridine with diborane, which was not characterized but undoubtedly was also aziridine-borane (IIa).

Preliminary experiments show that methylamine, dimethylamine and trimethylamine when reacted with sodium borohydride under the same conditions as were used for aziridine and N-methylaziridine, give the corresponding amine-boranes which have been characterized by their melting points and infrared spectra, and in the case of trimethylamine-borane by comparison with an authentic sample.

Work on this reaction is continuing and details will be reported elsewhere.

TABLE

NMR Data

	^{11}B (in $CHCl_3$)	^{1}H (in $CDCl_3$)[a]			
	J_{BH} cps	$-BH_3$	$-(CH_2)_2-$	$-CH_3$	J_{BH} cps
C_2H_8BN	91.3 ± 0.9	quartet 8.68 τ[b]	A_2B_2 7.88 τ[c]	-	92
$C_3H_{10}BN$	96.3 ± 0.7	quartet 8.49 τ[d]	7.96 τ[e]	singlet 7.4 τ	95

[a] TMS as the internal standard

[b] centre of the quartet; broad bands at 11.0 τ, 9.45 τ, 7.9 τ (obscured) and 6.4 τ

[c] centre of the symmetrical A_2B_2 pattern; multiplets at 7.63 τ and 8.16 τ

[d] centre of the quartet; broad bands at 10.9 τ, 9.3 τ, 7.7 τ (obscured) and 6.1 τ

[e] broadened singlet

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