Thioboranes: Their Use in the Synthesis of Borazines

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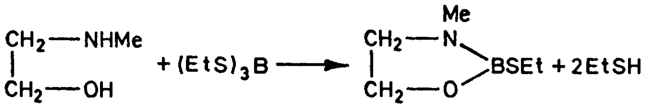
Summary Borazines, of type (A), have been synthesised in high yields by the reaction of a tristhioborane with hydroxy- and mercapto-amines; the mass spectrum of the cysteamine compound shows an unusual fragmentation pattern.

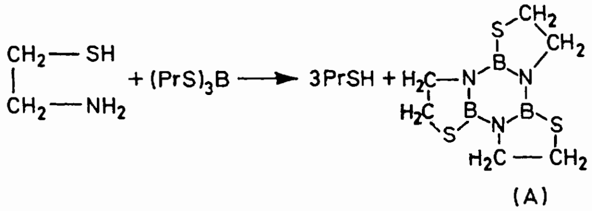
Thioboranes react readily with alcohols[1] and amines[2] to give the corresponding alkoxy- and amino-boranes. With difunctional organic compounds, such as mercapto-alcohols and secondary amino-alcohols, the corresponding organoboron heterocycle is obtained.[3] We find, however, that if one of the functional groups is a primary amino-group then the product of the reaction is not the expected heterocycle but a borazine. The scope of this reaction is exemplified by the borazines, prepared by this method, quoted in the Table. All the compounds have been characterised by analysis and i.r. and mass spectrometry. A typical reaction sequence is as follows. Cysteamine (7·7 g) and tri-n-propylmercaptoborane (23·4 g) were refluxed in dry benzene for 3 h. On removal of the volatile material the



Table

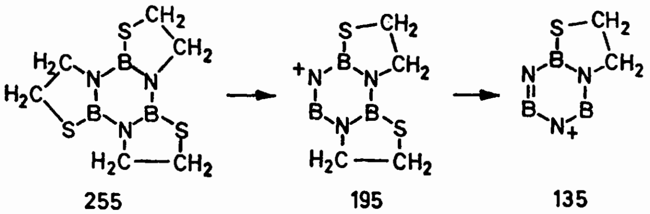
Reactants	Product	Yield	M.p. (°C)
(**1a**) + $(PrS)_3B$	(**2a**)	73	190
(**1b**) + $(PrS)_3B$	(**2b**)	82	150
(**1c**) + $(EtS)_3B$	(**2c**)	82	75
(**1d**) + $(EtS)_3B$	(**2d**)	82	102
(**1e**) + $(EtS)_3B$	(**2e**)	91	191
(**3**) + $(EtS)_3B$	(**4**)	74	172

residue on sublimation, (190°, 0·6 mmHg), afforded the borazine (A) (5·25 g, 73%). The ease of the reaction can be attributed to (*a*) the high affinity of boron for nitrogen and (*b*) the volatility of the mercaptan.

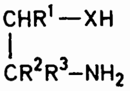


(A)

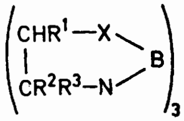
The mass spectra of these compounds show them to have high stability. That the formation of the borazine ring is most important was confirmed by the mass spectrum of the product of an incomplete reaction which showed that the borazine ring had been formed and that there were mercapto-groups still attached to the boron atom. However, the fragmentation pattern of the cysteamine compound is unusual. In the mass spectra of organoboron heterocycles the loss of the exocyclic group attached to the boron atom causes the disruption of the ring, owing to the planarity of the boron atom in such an environment, so that in such systems there has been as yet very little evidence of the existence of boronium ions.[4] However in the present case (Scheme), evidence is found for the loss of two exocyclic rings from the borazine nucleus before fragmentation of the nucleus.



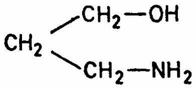
SCHEME



(1)

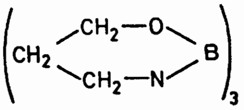


(2)



(3)

a; $R^1 = R^2 = R^3 = H$; $X = S$
b; $R^1 = R^2 = R^3 = H$; $X = O$
c; $R^1 = Me$; $R^2 = R^3 = H$; $X = O$
d; $R^1 = R^2 = H$; $R^3 = Me$; $X = O$
e; $R^1 = H$; $R^2 = R^3 = Me$; $X = O$



(4)

We thank the S.R.C. for financial support.

(*Received, October 28th,* 1971; *Com.* 1875.)

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