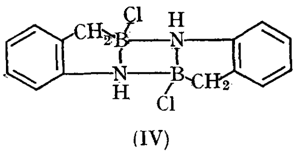
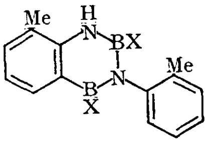
# Preparation of a Substituted 2,4-Dibora-1,3-diazarobenzene

By H. S. Turner, R. J. Warne and I. J. Lawrenson
(*National Chemical Laboratory, Teddington, Middx.*)

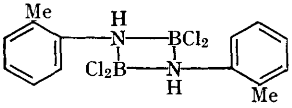
*o*-Toluidine–boron trichloride in boiling toluene loses hydrogen chloride in two successive first-order reactions to give first the borazene, *o*-tolylaminoboron dichloride, and then tri-*B*-chlorotri-*N*-*o*-tolylborazole, m.p. 212—213°, but when treated with triethylamine in the cold the main product is a compound (I) $C_{14}H_{14}B_2Cl_2N_2$, m.p. 120—122°, with the borazole as a minor product. This is not a borazyne dimer: it exhibits an N–H stretching band at 3445 cm.$^{-1}$ ($CCl_4$ solution). Compound (I) reacts with cold water to give a clear solution containing *o*-toluidine hydrochloride (1 mole), boric acid (1 mole), and the hydrochloride of 2-amino-3-methylphenylboronic acid (II) $C_7H_{11}BClO_2N$ (1 mole); on neutralisation, (II) is converted into an anhydride (III) $(C_7H_8ONB)_n$ which is insoluble in water. The value of $n$ in solution varies with the solvent and the concentration; it is least, ~1·8, in boiling dimethoxyethane. Hydrolysis of (I) in deuterium oxide gives *o*-toluidine with no C–D bond (i.r. spectrum); hydrolysis at 100° in deuterium oxide–deuterium chloride of (III) that has been prepared in water, gives boric acid (1 mole) and *o*-toluidine (1 mole) which has some ring C–D bonds but no methyl C–D bonds. It follows that the structure (IV) originally advanced[1] for compound (I) is incorrect and must be abandoned in favour of (V; X = Cl). Another compound containing this ring system, 2,4-diethyl-3-phenyl-2,4-dibora-1,3-diazaronaphthalene, has been prepared[2] from triethylborane, tetraethyldiborane, and phenylaminodiethylborane at 200° under pressure.



(IV)



(V)



(VI)

The physical evidence strongly favours structure

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[1] Report of the National Chemical Laboratory, H.M.S.O., 1963, 25.

[2] R. Köster and K. Iwasaki, A.C.S. Advances in Chemistry Series, 1964, **42**, 148.

(V). The $^{11}B$ chemical shifts of (V; X = Cl, $NMe_2$) and some relevant reference compounds are shown in the Table. Compound (V) clearly contains 3-co-ordinate boron. Only one peak is observed but it is likely that the shifts for the two boron atoms would be very similar. The chemical shifts of the "aromatic" and "aliphatic" protons in (V; X =Cl) ($\tau$2·83 and 7·7, 7·9) are very close to those in the borazole ($\tau$ 2·81 and 7·79). In both the integrated intensity of the two sets is ∼4 : 3; (IV) requires 2 : 1 whereas (V; X=Cl) requires 3½ : 3. The chemical shifts for the "aliphatic" protons are closer to those for toluene[3] (7·68) and *o*-xylene[3] (7·75) than for the methylene group of indene[3] (6·7). The two bands in (V; X=Cl) are more complex than in the borazole and in particular there are two peaks in the methyl region in (V) as would be expected for two methyl groups in different environments. The results for (V; $X=NMe_2$) and the corresponding borazole $(C_7H_7{\cdot}NBNMe_2)_3$ bear this out: in the spectrum of the former there is splitting of the *C*-methyl and *N*-methyl peaks. The C–H stretching regions of the infrared spectrum of (V; X=Cl), the borazole, and *o*-toluidine are almost identical, giving further strong evidence that (V) contains only methyl groups.

| Compound | Chemical shift (p.p.m.; $BCl_3$ = 0) | Band width (p.p.m.) |
|---|---|---|
| V; X=Cl | +16·0 | ∼20 |
| V; $X=NMe_2$ | +22·2 | ∼25 |
| *Three-co-ordinate* | | |
| $(o\text{-}C_7H_7{\cdot}NBCl)_3$ | +16·9 | ∼12 |
| $(o\text{-}C_7H_7{\cdot}NBNMe_2)_3$ | +16·7 | ∼27 |
| $(o\text{-}C_7H_7{\cdot}NBOH)_3$ | +26·8 | ∼20 |
| *Four-co-ordinate* | | |
| $(Me_2NBCl_2)_2$ | +38·5 | ∼7 |
| $(t\text{-}BuNHBCl_2)_2$ | +43·3 | |

It is possible that this unusual reaction takes place by way of the borazene dimer (VI), which on elimination of hydrogen chloride with the *ortho*-hydrogen of either ring, followed by electron redistribution and the loss of a second molecule of hydrogen chloride could give rise to (V).

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[3] "High Resolution N.M.R. Spectra Catalog". Varian Associates, Palo Alto, 1962.