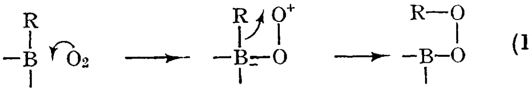
The Autoxidation of Optically Active 1-Phenylethaneboronic Acid

By Alwyn G. Davies and B. P. Roberts

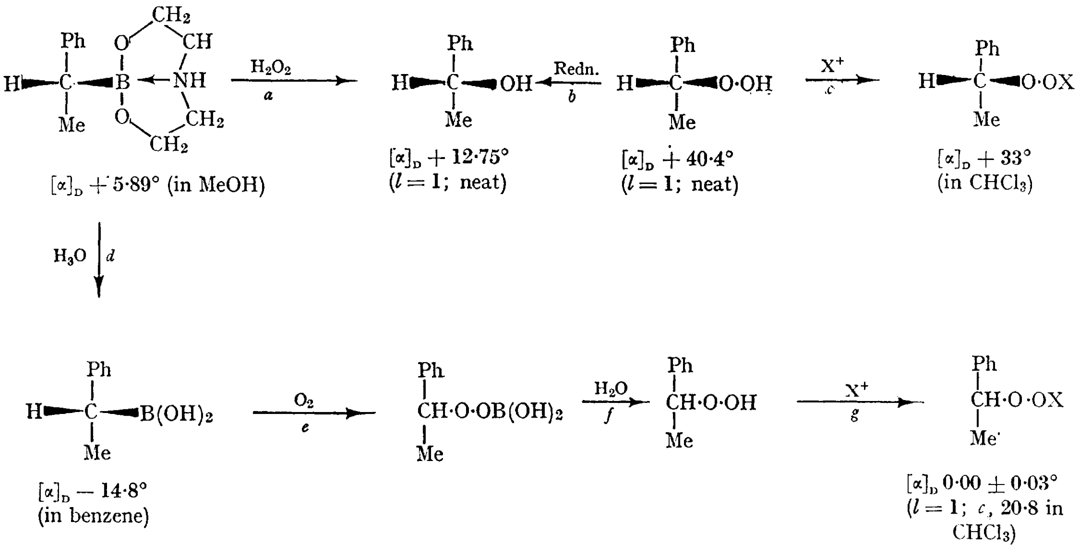
(*William Ramsay and Ralph Forster Laboratories, University College, London, W.C.*1)

The autoxidation of organoboranes to organoperoxyboranes is commonly accepted to involve co-ordination of oxygen to boron, accompanied or followed by nucleophilic 1,3-migration of the alkyl group from boron to oxygen (Equation 1).



(1)

The evidence is summarised in ref. 1. A radical chain mechanism is normally rejected because the autoxidation of tributylborane[2] and of butylboronic anhydride[3] is not inhibited by quinol, nor that of triethylborane[4] by iodine or methyl methacrylate. This argument loses its force, however, if, as now seems likely, organoboranes themselves are highly reactive towards radical reagents.[5] We have therefore investigated the stereochemistry of the autoxidation of optically active 1-phenylethaneboronic acid.[6]



Reaction scheme 2

(X = 9-xanthenyl. The rotatory power of the products of reactions 2*a*, *b*,[7] and *c*[7] have been derived, by proportion, from experiments using reactants of different optical purity.)

In benzene at room temperature, the boronic acid absorbs 0·93—0·98 mol. of oxygen to give the organoperoxyborane in high yield (Reaction 2*e*), and thence 1-phenylethyl hydroperoxide (Reaction 2*f*), which, in separate experiments, was isolated as such, or as its triphenylmethyl or 9-xanthenyl derivative[7] (Reaction 2*g*). In every case, the active boronic acid gave the racemic peroxide; typical results are given in reaction scheme 2.

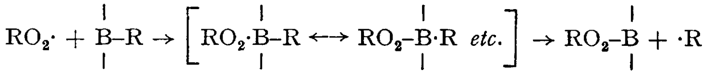
The boronic acid and the hydroperoxide are both optically stable in solution, and reactions 2*a*—*d*, *f*, and *g* all involve retention of configuration. The autoxidation must therefore take place with at least 99% racemisation, presumably *via* a three-co-ordinate carbon species. This was identified as a radical by its interaction with scavengers.

The autoxidation is first order in boronic acid (and of unknown order in oxygen), with a half-life at room temperature of about 6 min. The rate was not affected by the addition of *ca.* 1 mole % of phenyl-β-naphthylamine, thiophenol, 2,6-di-t-butyl-4-methylphenol, or diphenylpicrylhydrazyl, but phenothiazine had a slight inhibiting effect, and copper(II) *NN*-dibutyldithiocarbamate and galvinoxyl caused an induction period equal to about one and four half-lives respectively.

It appears then that the peroxide is in fact formed in a free-radical chain process, with the propagation steps as shown in Equations 3 and 4.

$$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{RO_2}\cdot \qquad (3)$$

This calls into question the mechanism of the autoxidation of other organoboron compounds, and of the organic derivatives of other metals such as magnesium, cadmium, zinc, and aluminium.



$$\mathrm{RO_2}\cdot + \overset{|}{\underset{|}{\mathrm{B}}}\text{–R} \rightarrow \left[\mathrm{RO_2}\cdot\overset{|}{\underset{|}{\mathrm{B}}}\text{–R} \longleftrightarrow \mathrm{RO_2}\text{–}\overset{|}{\underset{|}{\mathrm{B}}}\cdot\mathrm{R}\ \textit{etc.} \right] \rightarrow \mathrm{RO_2}\text{–}\overset{|}{\underset{|}{\mathrm{B}}} + \cdot\mathrm{R} \qquad (4)$$

(*Received, April 4th,* 1966; *Com.* 214.)

---

[1] A. G. Davies, *Progr. Boron Chem.*, 1964, **1**, 265.

[2] M. H. Abraham and A. G. Davies, *J. Chem. Soc.*, 1959, 429.

[3] O. Grummitt, *J. Amer. Chem. Soc.*, 1942, **64**, 1811.

[4] R. L. Hansen and R. R. Hamann, *J. Chem. Phys.*, 1963, **67**, 2868.

[5] D. S. Matteson, *J. Org. Chem.*, 1964, **29**, 3399; J. Grotewold and E. A. Lissi, *Chem. Comm.*, 1965, 21.

[6] D. S. Matteson and R. A. Bowie, *J. Amer. Chem. Soc.*, 1965, **87**, 2587.

[7] A. G. Davies and R. Feld, *J. Chem. Soc.*, 1956, 665.