Photochemical Reaction of Trialkylboranes in Alcohols. Convenient Synthesis of 2-Alkyl-1,3,2-dioxaborolanes

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Summary Irradiation of trialkylboranes (**1**) and propan-2-ol in n-hexane in air or nitrogen atmosphere produces the corresponding 2-alkyl-1,3,2-dioxaborolanes (**2**) in good yields; reactions in methanol and ethanol give similar results.

Trialkylboranes are exceptionally stable towards protic solvents such as water and alcohols under normal conditions,[1] and they are photochemically inactive in aliphatic solvents; *e.g.*, irradiation of tributylborane (0·27 M) in n-hexane for 10 h with a 500 W high-pressure mercury vapour lamp under nitrogen caused no reaction. In contrast, trialkylboranes readily react with alcohols when irradiated with u.v. light.

We observed previously that the major product of the photochemical reaction of ethyl 3-dicyclohexylborylacrylate in propan-2-ol was the dioxaborolane (**2a**).[2] We now report that dioxaborolanes can be obtained in high yields by the photochemical reaction of trialkylboranes with alcohols.

Although several methods are available for the synthesis of 2-alkyl-1,3,2-dioxaborolanes, *e.g.*, esterification of alkylboronic acid with diols,[3] transesterification of dialkyl alkylboronates with diols,[4] reaction of alkylboron dihalides with diols,[5] and reactions of trialkylboranes with glycol esters of boric acid[6] and with diols[1a] at high temperature, all require diols and not readily available boron compounds.† The trialkylboranes required for reactions reported here are readily obtained *via* hydroboration of olefins.[1b]

Irradiation of tricyclohexylborane (**1a**) (0·04 M) in propan-2-ol–n-hexane (4:1) for 20 h with a 500 W high-pressure mercury vapour lamp under nitrogen produced the dioxaborolane (**2a**) (68%), the structure of which was determined chemically and from spectral data.‡ Oxidation of (**2a**) with alkaline H_2O_2 produced cyclohexanol and 2,3-dimethylbutane-2,3-diol in equal amounts. The reaction of (**1a**) in propan-2-ol–n-hexane, in the dark, under nitrogen for 6 days did not produce (**2a**). Photochemical reactions of tricyclopentylborane (**1b**) and tri-n-octylborane (**1d**) with propan-2-ol produced the corresponding 2-cyclopentyl-(**2b**) and 2-octyl-dioxaborolane (**2d**), respectively (*ca.* 50%).

A quantitative yield of (**2a**) was achieved when the irradiation was carried out with air bubbling through the reaction mixture (*ca.* 3 mol of oxygen per mol of trialkylborane throughout). Other 2-alkyldioxaborolanes were similarly obtained in good yields. Irradiation of (**1b**), (**1c**), (**1d**), and (**1e**) in propan-2-ol–n-hexane produced (**2b**), (**2c**), (**2d**), and (**2e**) in 73, 50, 95, and 59% yields, respectively. Similar photochemical reactions of (**1a**) with ethanol and methanol produced the dioxaborolanes (**2f**) and (**2g**) in 50 and 35% yields, respectively, the former containing *trans*- and *cis*-isomers in a ratio of 66:34.

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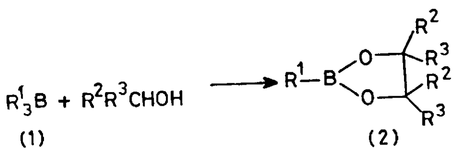
† Closely analogous dioxaboroles can, however, be readily obtained by hydroboration of olefins with catechol–borane (ref. 1b, p. 360, refs. therein).

‡ All products gave satisfactory analytical results and had the expected spectral data.



(1) (2)

	R^1	R^2	R^3
a;	Cyclohexyl	Me	Me
b;	Cyclopentyl	Me	Me
c;	Bu^s	Me	Me
d;	$n\text{-}C_8H_{17}$	Me	Me
e;	Pr^n	Me	Me
f;	Cyclohexyl	Me	H
g;	Cyclohexyl	H	H

Although the detailed mechanism of these photochemical reactions is not clear at present, the formation of dioxaborolanes may be explained as follows. It is well known that trialkylboranes readily react with oxygen to produce oxygen-containing boron compounds such as dialkyl alkylperoxyboranes, alkyl bis(alkylperoxy)boranes, and dialkyl alkylboronates.[7] Photolysis of alkylperoxyboranes would generate radicals, which in turn would abstract α-hydrogens of alcohols to form α-hydroxyalkyl radicals. Recombination of these radicals would produce a diol. Reaction of monoalkylboron compounds containing two boron–oxygen bonds with the diol would produce dioxaborolanes. That the present reactions follow this pathway is supported by the following results. (i) 2,3-Dimethylbutane-2,3-diol was actually isolated from the irradiated mixture of (**1**) in propan-2-ol. (ii) The reaction of (**1a**) in the dark in propan-2-ol with air bubbling did not produce (**2a**) and g.l.c. analysis of the reaction mixture indicated the formation of a new product which, although not fully characterised, is probably cyclohexyl bis(cyclohexylperoxy)borane or its alcoholysed product.[7] (iii) The reaction of (**1a**) in the dark in the presence of 2,3-dimethylbutane-2,3-diol with the introduction of air was found to produce (**2a**) in an almost quantitative yield. These results show that the intermediate boron compound, *e.g.* cyclohexyl bis(cyclohexylperoxy)-borane, is readily transesterified with the diol to give (**2a**).

The photochemical reaction under nitrogen probably proceeds *via* a different pathway from that under air. Under u.v. irradiation, some interaction between the vacant *p* orbital of the boron atom and that of the oxygen atom of the alcohol may play an important role in the initiation step.

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[1] (a) D. Ulmschneider and J. Goubeau, *Chem. Ber.*, 1957, **90**, 2733; (b) H. C. Brown, 'Boranes in Organic Chemistry,' Cornell University Press, Ithaca, 1972, p. 313.

[2] V. V. Chung, M. Tokuda, and M. Itoh, unpublished results.

[3] S. M. Darling, U.S.P. 2,710,252, 1955 (*Chem. Abs.*, 1955, **49**, 13640d); S. M. Darling, B.P. 785,724, 1957 (*Chem. Abs.*, 1958, **52**, 10562i).

[4] R. L. Letsinger and I. Skoog, *J. Amer. Chem. Soc.*, 1954, **76**, 4174.

[5] M. Wieberg and W. Künzel, *Z. anorg. Chem.*, 1974, **403**, 107.

[6] R. Köster, *Angew. Chem.*, 1959, **71**, 31.

[7] H. C. Brown, M. M. Midland, and G. W. Kabalka, *J. Amer. Chem. Soc.*, 1971, **93**, 1024; A. G. Davies and B. P. Roberts, *J. Chem. Soc.* (*B*), 1969, 311; P. G. Allies and P. B. Brindley, *ibid.*, 1969, 1127; J. R. Johnson and M. G. Van Campen, Jr., *J. Amer. Chem. Soc.*, 1938, **60**, 121.