Tetrahedron Letters No. 12, pp. 801-804, 1971. Pergamon Press. Printed in Great Britain.

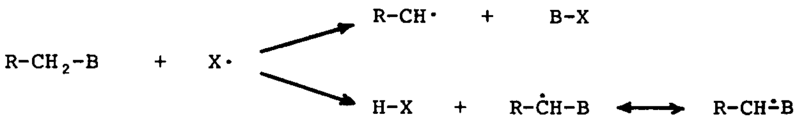
TRANSFER REACTIONS INVOLVING BORON. XXIII.
RADICAL REACTIVITY OF ALKANEBORONATES AND BORINATES[1]

Daniel J. Pasto and Kent McReynolds

Department of Chemistry, University of Notre Dame
Notre Dame, Indiana 46556

(Received in USA 17 February 1971; received in UK for publication 3 March 1971)

Organoboron derivatives can conceivably undergo two different types of reactions with a radical reagent: 1) Attack at boron with the displacement of another radical group; or 2) Abstraction of an α-hydrogen atom forming a stabilized α-boryl radical. The former type of reactivity has been demonstrated in the autoxidation of alkylboranes[2] and in the S_H2 displacement of an alkyl radical from a trialkylborane with t-butoxy radical.[3] The latter type of reactivity has been observed with the boronate ester 1;[4] however, the relative influence of the phenyl group versus the boron containing functional group could not be assessed.

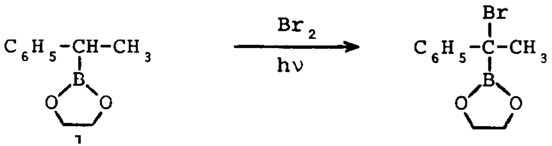


$$\text{R-CH}_2\text{-B} + \text{X}\cdot \longrightarrow \text{R-CH}\cdot + \text{B-X}$$

$$\text{R-CH}_2\text{-B} + \text{X}\cdot \longrightarrow \text{H-X} + \text{R-}\dot{\text{C}}\text{H-B} \longleftrightarrow \text{R-CH}\dot{=}\text{B}$$

$$\text{R}_3\text{B} + \text{t-BuO}\cdot \longrightarrow \text{R}_2\text{B-O-t-Bu} + \text{R}\cdot$$

$$(\text{R} = \text{CH}_3,\ \text{C}_2\text{H}_5,\ \text{n-C}_4\text{H}_9)$$

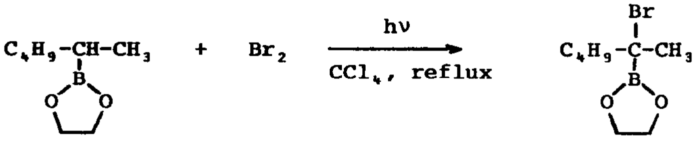


1

We have investigated the effect of alkyl group structure and substitution on boron in such radical reactions. Di-n-butyl and ethylene 1-hexaneboronate, prepared by the reaction of n-hexylmagnesium bromide with trimethyl borate at -78° followed by ester exchange with the appropiate alcohol as described previously,[4] do not react with bromine in refluxing carbon tetrachloride under ultraviolet irradiation. (In most of the radical bromination reactions involving organoboron derivatives normal laboratory light is sufficient to induce radical bromination). However, ethylene 2-hexaneboronate (**3**) readily undergoes radical bromination to produce **4** in quantitative yield (bp, 50°/0.05 mm; *Anal*. Calcd. for $C_8H_{10}BBrO_2$: C, 41.50; H, 6.91; B, 2.91; Br 31.6. Found: C, 41.5; H, 6.91; B, 2.88; Br, 31.6. nmr: δ 1.72 singlet (CH_3)).

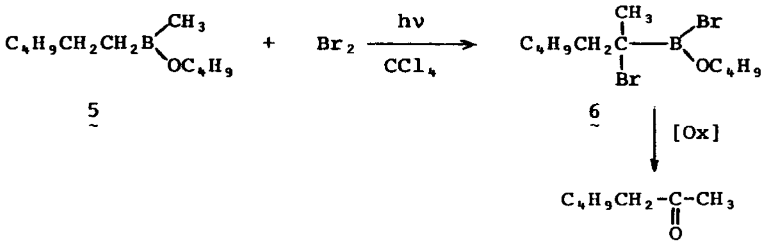
$$C_4H_9CH_2CH_2B(OR)_2 \quad + \quad Br_2 \xrightarrow[h\nu,\ \Delta]{} \quad \text{no reaction}$$

2 (R = *n*-C_4H_9, $-CH_2CH_2-$)



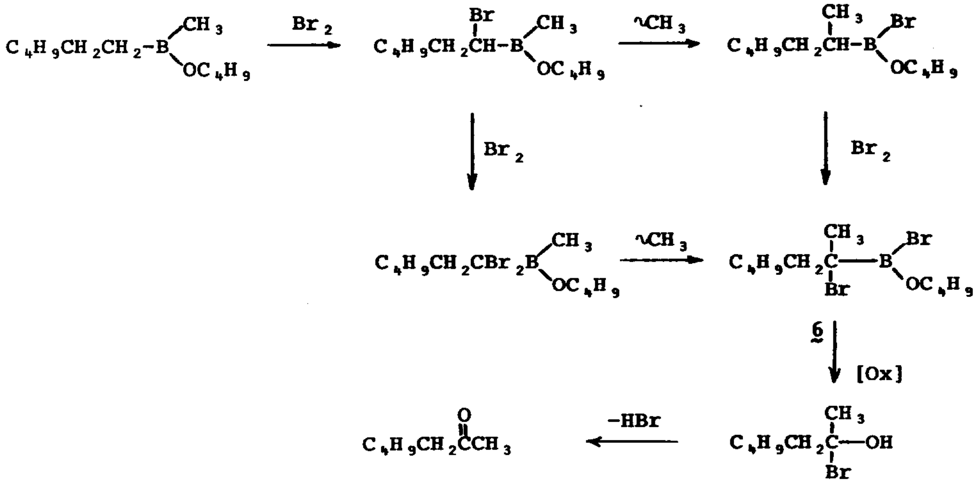
3 **4**

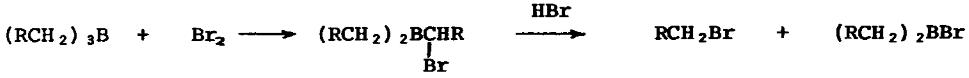
The effect of alkyl substitution on boron on the reactivity of organoboron derivatives in radical bromination was investigated with *n*-butyl methane-*n*-hexaneborinate (**5**) (prepared from **2** (R = *n*-C_4H_9) by treatment with nethyl magnesium bromide at -78°: bp 53-54°/10 mm; ^1H nmr, δ 0.31 singlet ($-B-C\underline{H}_3$); ^{11}B nmr, -53 ppm relative to capillary $BF_3\cdot(C_2H_5)_2O$; *Anal*. Calcd. for $C_{11}H_{25}BO$: C, 71.74; H, 13.68; B, 5.89. Found: C, 71.85; H, 13.69; B, 5.79). Surprisingly, the reaction of **5** led to the rapid consumption of two molar equivalents of bromine producing a product which on basic hydrogen peroxide oxidation gave 2-heptanone (70% yield) in addition to several other minor products.



5 **6**

The formation of the 2-heptanone is believed to occur as outlined below in the two possible reaction pathways. Attempts to distinguish between the two possible alternatives have not been successful. Alkyl group migrations from trigonal boron to carbon with displacement of halogen have not been previously observed; however, the migration of hydrogen from boron to carbon with the displacement of halogen has been observed in the hydroboration of vinyl halides.[5] Trialkylboranes react similarly with bromine under radical conditions wo give intermediates which react with the hydrogen bromide formed in the reactions to produce alkyl bromides and dialkylboron bromides.[6]





$$(RCH_2)_3B + Br_2 \longrightarrow (RCH_2)_2B\underset{\displaystyle Br}{CH}R \xrightarrow{HBr} RCH_2Br + (RCH_2)_2BBr$$

The treatment of compounds 2, 3, and 5 with Fenton's reagent (producing HO· and HOO·) does not lead to the abnormal oxidation reactions as observed with the phenylethaneboronates and bisboronates;[7] producing instead only the normal oxidation products 1- and 2-hexanol in excellent yield.

The present results indicate that the radical reactivity of organoboron derivatives is a sensitive function of the structure of the organic functional group(s) bonded to the boron atom, the nature of the substituents bonded to the boron atom, and the nature of the attacking radical species. The preferred attack by an oxygen radical at boron is undoubtedly controlled by the thermodynamics involved in the radical reactions; the formation of a B-O bond being much more exothermic than formation of a O-H bond. The preferred attack by bromine atom at the hydrogen atoms is a reflection of the low energy content of the B-Br bond.[8]

1) For part XXIII see D. J. Pasto and P. W. Wojtkowski, *J. Org. Chem.*, in press.

2) P. G. Allies amd P. B. Brindley, *J. Chem. Soc.*, *B*, 1126 (1969); A. G. Davies and B. P. Roberts, *ibid.*, 311 (1969) and references therein.

3) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 3942 (1969).

4) D. J. Pasto, J. Chow, and S. K. Arora, *Tetrahedron*, **25**, 1557 (1969).

5) D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2773 (1966).

6) C. F. Lane and H. C. Brown, *J. Amer. Chem. Soc.*, **92**, 7212 (1970).

7) D. J. Pasto, S. K. Arora, and J. Chow, *Tetrahedron*, **25**, 1571 (1969).

8) Research supported by the National Science Foundation, Grant No. GP-9552.