was proved to be greater than 90% pure, showing that LiCN yielded the cyano and not the isocyano derivative.

Diphenylchlorophosphine Sulfide (I).—This compound was prepared in a manner analogous to those of Rattenbury[7] and Jansen.[8] Diphenylchlorophosphine (44 g., 0.2 mole, $n^{21}{}_{\rm D}$ 1.6325) and phosphorous thiochloride (34 g., 0.2 mole) were heated at 125° until evolution of the phosphorous trichloride ceased. Distillation of the residual solution *in vacuo* yielded 48 g. (95%) of I, a clear colorless liquid, b.p. 152–155° (0.55 mm.), $n^{20}{}_{\rm D}$ 1.6563 (lit.[9] b.p. 155–160° at 0.3 mm.).

Diphenylcyanophosphine Sulfide (III). A. By II and Phosphorus Thiochloride.—Diphenylcyanophosphine (II) was prepared by the reaction of silver cyanide with diphenylchlorophosphine according to the method of Plets.[3] The colorless liquid (94% yield, b.p. 187–188° at 13.5 mm., $n^{20}{}_{\rm D}$ 1.6205, $d^{25}{}_4$ 1.1198) had elemental analyses in excellent agreement with the theoretical values. It did not solidify on standing (lit.[3] b.p. 170–175° at 15 mm., m.p. 39–40°).

Diphenylcyanophosphine (63 g., 0.3 mole) and phosphorus thiochloride (51 g., 0.3 mole, b.p. 125°) were heated at 102° until the by-product, phosphorus trichloride (b.p. 76°, 94%), ceased to distil. Distillation under reduced pressure yielded 56.8 g. (70%) of III as a colorless liquid, b.p. 149–151° (0.25 mm.), $n^{20}{}_{\rm D}$ 1.6414, $d^{25}{}_4$ 1.2023. This liquid solidified upon standing to give a white solid, m.p. 50.0–50.2°.

Anal. Calcd. for $C_{13}H_{10}NPS$: C, 64.18; H, 4.14; N, 5.76; P, 12.73; S, 13.18. Found: C, 64.25; H, 4.31; N, 5.72; P, 12.97; S, 13.00.

In other runs, the distillation was carried out also at 214–216° (9 mm.) to give the pure product. The infrared spectrum of the compound is consistent with the structure. The CN peak is observed at 2180 cm.$^{-1}$.

B. By I and Lithium Cyanide.—Anhydrous lithium cyanide (6.6 g., 0.2 mole) was added in portions under nitrogen to a solution of diphenylchlorophosphine sulfide (50 g., 0.2 mole) in 50 ml. of dry benzene. There was no immediate heat effect. After standing overnight at room temperature, the deep brown reaction mixture was heated at reflux for 1 hr. and then filtered by coarse fritted disk under nitrogen pressure. The solid was washed with two small portions of benzene. The combined filtrate and benzene washings were concentrated to a small volume. Distillation under reduced pressure yielded 33.7 g. (70%) of a colorless liquid, b.p. 213–214° (8.6 mm.), $n^{20}{}_{\rm D}$ 1.6393. The liquid solidified on standing to a white solid. The values for melting point, boiling point, index of refraction, and the infrared spectrum are the same as those of the compound prepared by reaction of II with phosphorus thiochloride.

The pot residue consisted of a nondistillable brown solid with an average molecular weight of 1360 and believed to be low molecular weight polymers of diphenylcyanophosphine sulfide.

Diphenylcyanophosphine Oxide.—Diphenylchlorophosphine oxide (23.6 g., 0.1 mole, b.p. 168–169° at 1.2 mm., $n^{20}{}_{\rm D}$ 1.6112) and anhydrous lithium cyanide (3.3 g., 0.1 mole) in 30 ml. of dry benzene were heated at reflux overnight. The reaction mixture was processed in the same manner as above. Distillation under diminished pressure gave 5.6 g. of starting material and 13.9 (59%) of an undistillable brown residue, m.p. 60–70°. This is the compound in the polymeric form to which these nitriles are readily converted.

Anal. Calcd. for $C_{13}H_{10}NOP$: N, 6.17; P, 13.63. Found: N, 5.83; P, 13.52.

Diphenyldicyanosilane.—Diphenyldichlorosilane (25 g., 0.1 mole, b.p. 99–100° at 0.3 mm.) was added dropwise to a suspension of anhydrous lithium cyanide (6.8 g., 0.206 mole) in 100 ml. of dry benzene. There was no heat evolution. After being heated at reflux overnight, the reaction mixture was processed in the same manner as above. Distillation of the residual liquid yielded 15.8 g. (67.5%) of a clear, colorless liquid, b.p. 118–122° (0.28 mm.), $n^{20}{}_{\rm D}$ 1.5636, $d^{24}{}_4$ 1.1146. The liquid was redistilled to give a main fraction, b.p. 122° (0.24 mm.), $n^{20}{}_{\rm D}$ 1.5626, $d^{26}{}_4$ 1.1067 (lit.[6] b.p. 142° at 2 mm., m.p. 46–48°, $n^{30}{}_{\rm D}$ 1.559932, $d^{30}{}_4$ 1.090432).

Anal. Calcd. for $C_{14}H_{10}N_2Si$: C, 71.75; H, 4.31; N, 11.35. Found: C, 71.36; H, 4.56; N, 10.56.

The infrared spectrum showed a major peak at 2180 cm.$^{-1}$ and a minor peak at 2260 cm.$^{-1}$. Separation by v.p.c. yielded two nearly equal components with the same absorption spectra except for the relative intensities of these two bands. It is possible, but as yet not proven, that the compound contains both cyano and isocyano groups.

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(7) K. H. Rattenbury, U. S. Patent 2,993,929 (1961).

(8) W. L. Jansen, U. S. Patent 2,662,917 (1953).

(9) W. A. Higgins, P. W. Vogel, and W. G. Craig, *J. Am. Chem. Soc.*, **77**, 1864 (1955).

Preparation, Characterization, and Reactions of Lithium and Sodium Tetraalkylboron Compounds

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Received November 30, 1963

Lithium and sodium tetraalkylboron compounds have been prepared by the reaction of alkyllithium and alkylsodium reagents with trialkylboranes. These tetraalkylboron compounds show extreme reactivity toward air and were therefore identified by the formation of stable tetramethylammonium and tetrabutylphosphonium derivatives. Unusual infrared and n.m.r. absorption peaks at 2750–2800 cm.$^{-1}$ and 10–10.5 p.p.m., respectively, were present in the spectra of the tetravalent boron compounds. It was shown that these peaks arise from methylene groups adjacent to negative boron atoms. The stability of lithium tetraalkylboron compounds and tetramethylammonium tetrabutylboron in water, acetic acid, and sodium hydroxide solutions was studied. Hydrolysis with 20% acetic acid results in a rapid loss of 1 mole of alkane followed by a slow hydrolysis of the resultant trialkylborane. Air oxidation of lithium tetrabutylboron in tetrahydrofuran at 35° yielded 48% 1-butanol and 3% *n*-butyraldehyde of the theoretical amounts along with a 15% recovery of *n*-butane. The possible routes to these oxidation products are discussed.

Although the synthesis and chemistry of tetraaryl or mixed tetraarylalkylboron compounds have received considerable study,[1] relatively little is known about purely aliphatic tetravalent boron compounds. Over 30 years ago, Thompson and Stevens[2] reported an unsuccessful attempt to prepare these compounds. Soon after this report Johnson and his co-workers[3] observed a positive reaction when they combined tributylborane and *n*-butyllithium. In 1940 Schlesinger and Brown[4] obtained a white solid from the reaction of equimolar amounts of ethyllithium and trimethylborane, to which they assigned the formula $LiC_2H_5{\cdot}B(CH_3)_3$. In the ensuing years Hurd[5] prepared lithium tetramethylboron, and Parsons and co-workers[6] prepared lithium

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(1) M. F. Lappert, *Chem. Rev.*, **56**, 1035 (1956).

(2) T. Thompson and T. S. Stevens, *J. Chem. Soc.*, 556 (1933).

(3) J. R. Johnson, H. R. Snyder, and M. G. Van Campen, Jr., *J. Am. Chem. Soc.*, **60**, 115 (1938).

(4) H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

(5) D. T. Hurd, *J. Org. Chem.*, **13**, 711 (1948).

(6) T. D. Parsons, M. B. Silverman, and D. M. Ritter, *J. Am. Chem. Soc.*, **79**, 5091 (1957).

TABLE I

TETRAMETHYLAMMONIUM AND TETRABUTYLPHOSPHONIUM DERIVATIVES OF TETRAALKYLBORON COMPOUNDS

Reaction: $MR'BR_3 + CBr \longrightarrow CR'BR_3 + MBr$
$M = Li$ or Na
$R' = C_4H_9$ or $C_{12}H_{25}$
$R = C_2H_5$ or C_4H_9
$C = (CH_3)_4N$ or $(C_4H_9)_4P$

	% yield, $(CH_3)_4NR'BR_3$	M.p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
MR^1BR_3			Calcd.	Found	Calcd.	Found	Calcd.	Found
$Li(C_2H_5)_3BC_4H_9$	89	103–105 dec.	73.3	72.8	15.8	15.6	6.11	6.03
$Li(C_4H_9)_4B$	91	110–112 dec.	76.6	76.3	15.4	15.5	4.47	4.47
$Li(C_2H_5)_3BC_{12}H_{25}$	84	Oil	77.2	77.0	15.4	15.2	4.10	3.97
$Li(C_4H_9)_3BC_{12}H_{25}$	87	Oil	79.0	77.9	15.2	15.0	3.29	3.33
$Na(C_4H_9)_4B$	78	110–112 dec.	76.6	76.2	15.4	15.7	4.47	4.40
$Na(C_2H_5)_3BC_{12}H_{25}$	88	Oil	77.2	77.5	15.4	15.2	4.10	4.02
	% yield, $(C_4H_9)_4PR'BR_3$						Phosphorus, %	
							Calcd.	Found
$Li(C_2H_5)_3BC_4H_9$	65	76–78 dec.	75.3	74.9	14.6	14.3	7.47	7.35
$Li(C_4H_9)_4B$	80	52–55 dec.	77.1	77.1	14.6	14.4	6.21	6.10
$Li(C_2H_5)_3BC_{12}H_{25}$	75	Oil	77.5	78.3	14.5	14.0	5.88	5.70
$Li(C_4H_9)_3BC_{12}H_{25}$	68	Oil	78.6	78.9	14.5	14.2	5.07	4.95

trimethylpropenylboron by this method. The structure of all these products was inferred from the stoichiometry of the reactions and some brief hydrolysis studies. More recently Honeycutt and Riddle[7] reported the preparation of several sodium tetraalkylboron compounds by the novel reaction of sodium triethylborohydride with an α-olefin. Assignment of structures was based on partial elemental analyses, hydrolysis data, and infrared spectra. Ethereal solvents, which give solvated products, were generally used in this reaction system.

Despite this past work, a detailed study of metal tetraalkylboron compounds had not been made. The purpose of this paper is to report the syntheses, characterization, and some of the chemical and physical properties of nonsolvated lithium and sodium tetraalkyl boron compounds.

Preparation.—Attempts to use the method of Honeycutt and Riddle to prepare sodium tetraalkylboron compounds resulted in impure materials which could not readily be purified. However, the direct reaction of an organometallic with trialkylborane in hydrocarbon diluent proceeds smoothly to give the desired MBR_4 compounds,[8] which are easily purified.

$$MR' + R_3B \xrightarrow{n\text{-alkane}} MR_3BR'$$

Compounds prepared
I, $Li(C_2H_5)_3BC_4H_9$
II, $Li(C_4H_9)_4B$
III, $Li(C_2H_5)_3BC_{12}H_{25}$
IV, $Li(C_4H_9)_3BC_{12}H_{25}$
V, $Na(C_4H_9)_4B$
VI, $Na(C_2H_5)_3BC_{12}H_{25}$

Sodium tetraalkylborons, prepared in this manner, are partially soluble in hexane and can be separated from the insoluble alkylsodium reagents by extraction. This resulted in low yields (20–30%) of the pure sodium products. The homogeneous reaction of organolithium and trialkylboron reagents in hexane or pentane provided an 80–95% recovery of insoluble $LiBR_4$ compounds by simple filtration and washing under an inert atmosphere.

Identification.—Since lithium and sodium tetraalkylboron compounds are quite reactive to air, direct analysis of these materials is difficult. It was found, however, that analyzable derivatives of these compounds could be easily prepared in high yields. Thus, water solutions of both lithium and sodium compounds afforded insoluble derivatives upon treatment with either tetramethylammonium or tetrabutylphosphonium bromides. The results from these reactions are summarized in Table I.

Since high yields[9] of pure derivatives are obtained in all cases, there can be little doubt that the original organoboron compounds are indeed pure. Both the ammonium and phosphonium derivatives could be transferred and recrystallized in air without appreciable decomposition. Apparently, the nature of the cation, besides changing the water solubility of the tetralkyl boron compounds, has a remarkable effect on the reactivity of these compounds with oxygen.

Additional evidence for the purity and structural assignments in this class of metal tetraalkylboron compounds was obtained from infrared and nuclear magnetic resonance (n.m.r.) spectra. Table II shows the pertinent infrared absorptions. Of particular interest is the strong absorption found in all these compounds at 2760–2780 cm.$^{-1}$. Peaks in this region immediately suggest a carbon–hydrogen stretching frequency that is shifted by 100–150 cm.$^{-1}$ from the normal region.[10] Absorptions quite similar to these reported here have been observed previously with methyl-, ethyl-, and phenyllithium.[11] To account for this low C–H stretching frequency, West and Glaze postulated association[12] of alkyllithiums to form electron-deficient lithium–carbon–lithium bonds. However, an explanation of this type is not applicable to the tetraalkylboron system for several reasons. First, the negative charge in these compounds represents an ionic charge, not a free

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(7) J. B. Honeycutt, Jr. and J. M. Riddle, *J. Am. Chem. Soc.*, **83**, 369 (1961).

(8) All of the alkyl groups in our compounds are unbranched. The prefix *n* is generally omitted in the text for the sake of simplicity without misleading the reader.

(9) Slightly lower yields of the phosphonium–boron compounds, compared to yields of the ammonium–boron compounds, are probably due to the greater water solubility of the former.

(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Company, London, 1958, p. 13.

(11) R. West and W. Glaze, *J. Am. Chem. Soc.*, **83**, 3580 (1961).

(12) Organolithium reagents have been found to be associated in solution and in vapor phase: *cf.* T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *ibid.*, **84**, 1371 (1962), and references therein, for a discussion of this phenomenon.

pair of electrons. Therefore, it is difficult to write reasonable structures to utilize the lithium orbitals in covalent bonding. Secondly, the tetramethylammonium and tetrabutylphosphonium tetraalkylboron compounds also have strong low frequency C–H absorptions and, since the ammonium and phosphonium cations could not possibly be involved in covalent bonding, another explanation is necessary to explain the observed infrared absorption.

TABLE II

MAJOR INFRARED ABSORPTIONS OF TETRAALKYLBORON COMPOUNDS,[a] CM.$^{-1}$

$Li(C_2H_5)_3B(C_4H_9)$	$Li(C_4H_9)_4B$	$Li(C_2H_5)_3BC_{12}H_{25}$
2940	2940	2940
2870	2870	2870
2770	2770	2760
1465	1465	1465
1375	1380	1380
1075	1095	1315
1060	1065	1080
1040	1040	1060
	740	890
		720

$Li(C_4H_9)_3BC_{12}H_{25}$	$Na(C_4H_9)_4B$[b]	$Na(C_2H_5)_3BC_{12}H_{25}$[b]
2940	2940	2940
2870	2870	2870
2760	2780	2770
1465	1465	1465
1380	1375	1380
1300	1095	1070
1095	1010	1040
1060	990	870
740	740	730
720		720

[a] Bands observed in Nujol and/or Kel-F mulls. All absorptions have a minimum absorbance value of 0.4 relative to the strong peak ($A = 1.4$) of $Li(C_4H_9)_4B$ at 2770 cm.$^{-1}$. [b] Samples were run as melts.

The most logical effect of the negative boron atom would be to donate charge inductively to the carbon skeleton, causing an infrared shift of the C–H stretching frequency. The literature reveals little information on the effect of negative atoms or groups on the C–H stretching mode.[13] We have, however, evidence that the absorption at 2770 cm.$^{-1}$ is due to the C–H stretching frequency of methylene groups adjacent to the negative boron atom. This information was gained by studying a series of tetrasubstituted boron compounds in which the number of methylene groups adjacent to the negative boron atom was varied. These compounds and their extinction coefficients are shown in Table III.

It is clear that the intensity of the absorption in the 2800-cm.$^{-1}$ region decreases progressively to zero as the number of α-methylene groups is varied from four in II to none in IX. This data provides strong evidence for the postulate that the α-methylene groups are responsible for the absorptions under discussion.[14,15]

TABLE III

EXTINCTION COEFFICIENTS OF TETRASUBSTITUTED BORON COMPOUNDS[a]

	No. of α-methylene groups	Infrared max., cm.$^{-1}$	Extinction coefficient, l./mole-cm.
$Li(C_4H_9)_4B$ (II)	4	2785	197 ± 10
$Li(C_4H_9)_3BC_6H_5$ (VII)	3	2800	157 ± 2
$Li(C_4H_9)B[C_6H_5]_3$ (VIII)	1	2800	28 ± 3
$Na(C_6H_5)_4B$ (IX)	0	None from 2750–2850	0

[a] Acetonitrile was used as a solvent for the infrared study. This solvent shifts the absorptions of tetrasubstituted boron compounds to slightly higher frequencies (10–20 cm.$^{-1}$) compared to the absorptions observed in Nujol mulls.

The transmission of negative charge from the boron atom to the α-methylenes is readily shown by the n.m.r. spectra of the tetraalkylboron complexes. Three bands were observed in the n.m.r. spectrum of lithium tetrabutylboron. Bands 1 and 2 were overlapping from 8.95 to 9.55 p.p.m.[16] and band 3 was separate and centered at 10.3 p.p.m. Integration shows a proton ratio of 7:2 for the ratio of the combined bands 1 and 2 compared to 3. From this information it is plausible that band 3 represents the α-methylene groups, and absorptions between 8.95 and 9.55 p.p.m. represent the propyl skeleton. Further evidence for this is shown in the n.m.r. spectrum of lithium tetraethylboron, where the methylene peak is centered at 10.5 p.p.m. and the methyl peak at 9.8 p.p.m. The absorptions at 10.3 and 10.5 p.p.m. are shifts of 1.6 and 1.8 p.p.m. from the methylene absorptions of normal hydrocarbons. A shift above 10 p.p.m. and at a higher field than methyl absorptions is typical of methylenes adjacent to negative charges and attached to metals.[17] All of the peaks are complex due to large J/δ values and to boron–hydrogen spin–spin coupling.[18]

The combined infrared and n.m.r. absorption spectra clearly show the pronounced influence of the negative boron atom on the α-methylene groups.

The band at 1100 cm.$^{-1}$ in Table II is most probably due to a B–C stretching frequency. Other B–C ab-

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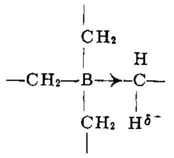
(13) L. J. Bellamy [*J. Chem. Soc.*, 4221 (1955)] states that the $-CH_2-$ deformation frequencies of $CH_2{=}CRR'$ compounds decrease as the electronegativity of the R and R′ groups increase. In this study only groups with −I effects were used. The effect of electron-donating and -withdrawing groups on the OH stretching frequency of carboxylic acids is well known [*cf.* J. D. S. Goulden, *Spectrochim. Acta*, **6**, 129 (1954)]. Whether these known effects would be applicable to a predicted change in C–H stretching frequency is open to debate.

(14) The reason for low frequency infrared shifts is not clear. One possible explanation for the C–H shift of tetraalkylboron compounds involves contributing hydride structures of the type shown. Hydride character in the tetraalkylboron compounds was originally proposed and discussed by G. Wittig [*Angew. Chem.*, **70**, 65 1958)]. Evidence that these structures are possible is found in the fact that lithium tetrabutylboron is a good hydride donor [H. Jäger and G. Hesse, *Chem. Ber.*, **95**, 345 (1962)].



$$-CH_2-\overset{\overset{|}{CH_2}}{\underset{\underset{|}{CH_2}}{B}}\rightarrow\overset{H}{\underset{H^{\delta-}}{C}}-$$

(15) (a) Because of the difference in inductive effect between phenyl and *n*-butyl there is no direct proportion between the extinction coefficients of compounds II through IX and the number of α-methylene groups. (b) Interestingly enough, Honeycutt and Riddle,[7] who reported the infrared spectrum of sodium tetraethylboron, did not observe the strong absorption at 2770 cm.$^{-1}$. This is due to masking of the absorption by complexed solvent. When our compounds were allowed to come in contact with diethyl ether, the band at 2770 cm.$^{-1}$ was obscured by ether bands.

(16) Measured relative to tetramethylsilane (10 p.p.m.) as an *external* reference.

(17) G. Frankel, D. G. Adams, and J. Williams, *Tetrahedron Letters*, **12**, 767 (1963), and references cited therein.

(18) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 298.

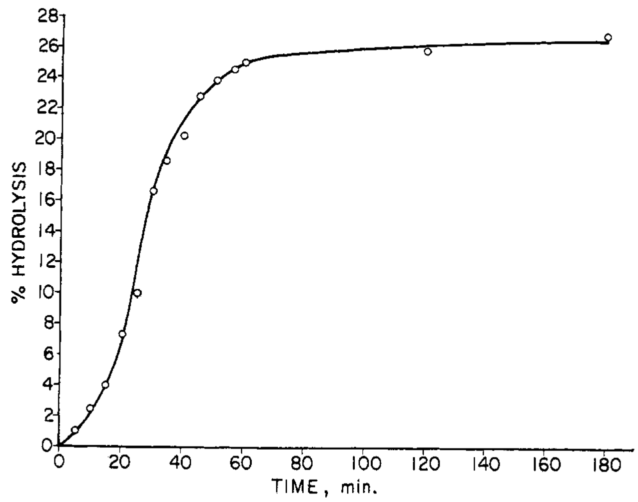


Fig. 1.—Hydrolysis of $Li(C_4H_9)_4B$ with 20% acetic acid at 60°.

sorptions in this general region have been observed in triethylborane and trimethylborane.[19]

Hydrolysis.—The stability of tetraalkylboron compounds in water, acids, and sodium hydroxide solutions was studied. There is ambiguity in the literature concerning the water stability of the tetravalent boron compounds. Honeycutt and Riddle[7] report that sodium tetraethylboron is hygroscopic and stable in water. Schlesinger and Brown[4] state that lithium triethylbutylboron dissolves in water and slowly evolves a gas; Hurd[5] claims that lithium tetramethylboron decomposes vigorously with a drop of water.

Our hydrolysis results are summarized in Table IV. The lithium tetraalkylboron compounds and tetramethylammonium tetrabutylboron were studied in detail because they represented extremes in reactivity toward water. All of the tetraalkylboron compounds were fairly stable in water, decomposing from 0.5 to 13% at 35° in 16 hr. Base did not have an appreciable effect on their stability, causing only a maximum of 3% change in the per cent hydrolysis. Acetic acid causes a rapid hydrolysis of the tetraalkylboron compounds at 60°. For example, the hydrolysis of lithium tetrabutylboron with 20% acetic acid evolved 25% of the theoretical volume of butane within 1 hr. An additional 2-hr. reaction time resulted in a total of 27% hydrolysis (see Fig. 1). From this information, and the similarity of this reaction to those of the other tetraalkylboron compounds, it is reasonable that the hydrolysis of these compounds involves a rapid protonation and loss of alkane, followed by a slow hydrolysis of the resulting trialkylboranes (reactions 1 and 2).

$$MBR_4 + AcOH \xrightarrow{\text{fast}} MOAc + R_3B + RH \quad (1)$$

$$R_3B + AcOH \xrightarrow{\text{slow}} 3RH + B(OAc)_3 \quad (2)$$

Table IV

Per Cent Hydrolysis of Tetraalkylboron Compounds[a]

Tetraalkylboron compound	NaOH solution H_2O 35°, 16 hr.	pH 10 35°, 16 hr.	20% HOAc 60°, 1 hr.
$Li(C_2H_5)_3B(C_4H_9)$			29.2
$Li(C_4H_9)_4B$	13	15.9	24.5
$Li(C_2H_5)_3BC_{12}H_{25}$	12[b]	12.5[b]	33.1[c]
$Li(C_4H_9)_3BC_{12}H_{25}$	12.8[b]	11.1[b]	36.5[c]
$(CH_3)_4NB(C_4H_9)_4$	0.45	0.0	55[d]

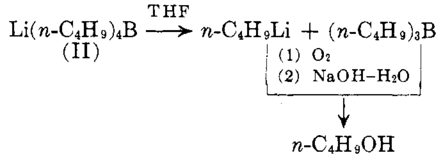
[a] Per cent hydrolysis is calculated on the basis of 4 moles of theoretical alkane for each mole of tetraalkylboron compound. [b] Based on per cent gas only. [c] Based on per cent gas and dodecane. [d] The extreme sensitivity of tetramethylammonium tetrabutylboron to acetic acid has not been studied.

The exact nature of the initial proton transfer and loss of alkane cannot be defined from the available data; however, it is plausible that proton attack occurs at the electron dense α-carbon atom with accompanying loss of alkane.[20]

Correcting for statistical factors, the relative rate of bond cleavage of ethyl to butyl, ethyl to dodecyl, and butyl to dodecyl, is 1.75 ± 0.20, 1.00 ± 0.10, and 0.95 ± 0.10, respectively.

Oxidation.—The lithium and sodium tetraalkylboron compounds are extremely reactive to both dry and moist air. Trialkylboranes react spontaneously with oxygen due to the ease of coordination between oxygen and the empty boron orbital.[21] This, of course, is impossible with tetravalent boron compounds and therefore some other pathway must be followed.

The oxidation of lithium tetrabutylboron (II) in tetrahydrofuran (THF) at 35° for 16 hr. followed by hydrolysis yielded 48 and 3%, respectively, of the theoretical amounts of 1-butanol and *n*-butyraldehyde. The other liquid products totaled only 1.4%. In addition, we obtained a 15% recovery of *n*-butane; and no other gaseous products were found. This relatively clean free-radical oxidation could be explained by assuming an equilibrium of II with butyllithium and tributylborane, followed by oxidation and basic hydrolysis.[22,23] However, there is strong evidence that this mechanism is not operative in our system. Lithium



$$\underset{\text{(II)}}{Li(n\text{-}C_4H_9)_4B} \xrightarrow{\text{THF}} n\text{-}C_4H_9Li + (n\text{-}C_4H_9)_3B \xrightarrow[\text{(2) NaOH-H}_2\text{O}]{\text{(1) O}_2} n\text{-}C_4H_9OH$$

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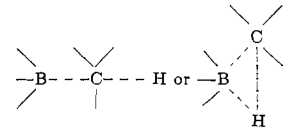
[19] W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *J. Chem. Phys.*, **28**, 777, 781 (1958).

[20] Comparing hydrolysis reactions of tetraalkylboron compounds with those of sodium borohydride [R. E. Davis, E. Bromels, and C. L. Kibby, *J. Am. Chem. Soc.*, **84**, 885 (1962)] and sodium tetraphenylboron [J. N. Cooper and R. E. Powell, *ibid.*, **85**, 1590 (1963); V. A. Simon, *Dissertation Abstr.*, **13**, 1534 (1962)] provides some basis for these arguments. Cooper and Powell found no evidence for tetraphenylboric acid [$HB(C_6H_5)_4$] in their studies with tetraphenylboron. From this experiment it is highly unlikely that a five-coordinated boron species exists during the hydrolysis of tetraalkylboron compounds. The work of Simon as well as that of Cooper and Powell provides evidence that proton attack in the hydrolysis of tetraphenylboron occurs at the α-carbon atom. It is reasonable that the tetraalkylboron system should follow the same path. Finally, Davis, *et al.*, state that a DBH_4 species is not present during the reaction of sodium borohydride with deuterium oxide, but instead propose two activated complexes in which H-D bond formation is proceeding with B-H bond breaking in either a linear or triangular arrangement. A similar type complex, such as is presented, is a probable intermediate in the hydrolysis of tetraalkylboron compounds.



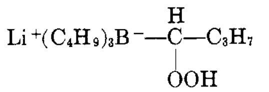
[21] S. B. Mirviss, *J. Am. Chem. Soc.*, **83**, 3051 (1961), and references cited therein.

[22] The major product (49%) in the oxidation of tributylboron by oxygen in THF is 1-butanol after hydrolysis (see ref. 21).

[23] It is well known that butyllithium reacts with air to produce 1-butanol upon hydrolysis: *cf.* E. Möller and T. Töpel, *Ber.*, **72**, 273 (1939).

tetrabutylboron does not react with benzyl chloride under the same solvent and temperature conditions used for the oxidation. We would certainly expect to obtain transmetalation or alkylation products at 35° in THF if butyllithium were in equilibrium with II.[24] Moreover, even at longer reaction times, II does not react with benzophenone. Some other path must then be operative. As n-butyl alcohol was obtained in high yields without the formation of iso- or *sec*-butyl alcohol, an initial reaction at the α-carbon atom, either by insertion of oxygen between boron and carbon, or by hydroperoxide formation, would give rise to likely precursors to our products. No attempt has been made at this time to differentiate between these two intermediates.[25]

$Li^+(C_4H_9)_3B^-—O—O—C_4H_9$ X



$$Li^+(C_4H_9)_3B^-—\overset{H}{\underset{OOH}{C}}—C_3H_7$$

XI

Experimental

Melting points of air-sensitive reagents were obtained in sealed tubes and are uncorrected. All compounds reactive to air and moisture were handled in an argon atmosphere. Hydrocarbon solvents were dried and distilled from sodium and stored over calcium hydride. Tri-n-butylborane and triethylborane (Callery Chemical Co.) were distilled before use.

n-Dodecyllithium was prepared using a modification of a procedure of Meals.[26] In a typical preparation, lithium metal dispersion (Foote Chemical Co., 1.10 moles, 20% excess) was placed in a 1-l. three-necked flask equipped with an addition funnel, condenser, thermometer, argon inlet, and stirrer. The flask was modified to include a stopcock at the bottom. The lithium metal was washed with 100 ml. of benzene and two 50-ml. portions of hexane. Five milliliters of n-dodecyl chloride in 20 ml. of hexane was added and the mixture was heated to gentle reflux and stirred. The reaction usually started with a darkening of the lithium metal and a rise in temperature. The remaining n-dodecyl chloride (0.50 mole) was diluted with enough hexane to make a 1 M solution and added over 1 hr. to the mixture maintained at 65° by heating. After addition, the mixture was transferred to centrifuge bottles, covered with rubber serum caps, and centrifuged for 15–30 min. The supernatant liquid was removed with a syringe. The remaining solid in each bottle was extracted with two 50-ml. portions of hexane. Titration of the n-dodecyllithium by the Gilman procedure showed a 55–62% yield.

Preparation of Lithium Tetraalkylboron Compounds.—The lithium tetraalkylboron compounds were prepared by direct reaction of an organolithium reagent and a trialkylborane in hexane or pentane diluent. The following example illustrates the general procedure. Butyllithium (Foote Mineral Co., 0.10 mole) was placed in a 1-l. three-necked flask equipped with a stirrer, addition funnel, condenser, thermometer, and argon inlet. Tri-n-butylborane (0.10 mole, 18.2 g., 23.4 ml.) in an equal volume of hexane was added at room temperature with stirring. Formation of a white solid was immediately visible as the temperature rose to 30–40°. After addition, the heterogeneous mixture was heated to 45° and stirred for 1 hr. After cooling, the resultant solid was filtered, washed with five 50-ml. portions of hexane, and dried at 45° (0.1 mm.) for 2 hr.

The range of yields and melting points of the lithium tetraalkylboron compounds are shown in Table V.

TABLE V

	Compound	% yield	M.p., °C.
I,	$Li(C_2H_5)_3B(n\text{-}C_4H_9)$	92–93	122 dec.
II,	$Li(n\text{-}C_4H_9)_4B$	85–92	205 dec.
III	$Li(C_2H_5)_3B(n\text{-}C_{12}H_{25})$	77–85	93 dec.
IV,	$Li(n\text{-}C_4H_9)_3B(n\text{-}C_{12}H_{25})$	55–64[a] 86[b]	142 dec.

[a] Yield after washing the product with hexane. [b] Yield after washing the product with pentane. The higher yield of product using pentane as a wash solvent shows the lower solubility of IV in pentane.

Preparation of Lithium Triphenylbutylboron and Lithium Tributylphenylboron.—Triphenylborane (Aldrich Chemical Co.) was sublimed at 140° (0.09 mm.) to yield a white solid, m.p. 139–140°, lit.[27] m.p. 142–142.5°. To 2.5 g. (0.01 mole) of sublimed triphenylborane dissolved in 20 ml. of benzene, 6.4 ml. of 1.6 M butyllithium in 40 ml. of hexane was added. A white solid was formed which was filtered, washed with two 50-ml. portions of pentane, and dried at 30° (0.1 mm.) for 1 hr. A total of 1.8 g. (59%) of lithium triphenylbutylboron was recovered, m.p. 325° dec.

Anal. Calcd. for $C_{22}H_{24}BLi$: C, 86.3; H, 7.92. Found: C., 86.7; H, 7.72.

To 5.4 ml. (0.010 mole) of 1.84 M phenyllithium in 20 ml. of benzene, a solution of 2.0 g. (0.011 mole) of tributylboron in 40 ml. of benzene was added. No precipitate was formed, but the temperature rose to 32°, indicating a positive reaction. The solution was heated at 40° for 1 hr., cooled, and evaporated under nitrogen. The liquid product was further evaporated at 40° (0.1 mm.) for 24 hr. A total of 2.4 g. (91%) of lithium tributylphenylboron was recovered.

Anal. Calcd. for $C_{18}H_{32}BLi$: C, 81.6; H, 11.8. Found: C, 81.2; H, 11.5.

Preparation of Sodium Tetraalkylboron Compounds.—n-Butylsodium and n-dodecylsodium were prepared from n-alkyl chloride and sodium metal dispersion in n-octane by Morton's procedure.[28] Carbonation of the alkylsodium reagents indicated yields of 50–60%.

The general procedure for preparing sodium tetraalkylboron compounds is illustrated for sodium triethyldodecylboron. To 0.05 mole of n-dodecylsodium suspended in 150 ml. of n-octane was added 4.8 g. (0.05 mole) of triethylborane in 50 ml. of n-octane. A slight rise in temperature (5°) indicated the reaction had started. The mixture was stirred with a high speed stirrer for 1 hr. A thick, pasty material resulted and this was transferred to centrifuge bottles, capped, and centrifuged for 0.5 hr. The supernatant liquid was drawn off and discarded. The resultant solid was extracted with two 100-ml. portions of heptane. A total of 4.3 g. (32%) of white, solid material was recovered after drying at 40° (0.1 mm.) for 2 hr.

The results of these preparations follow.

	Compound	% yield	M.p. dec., °C.
V,	$Na(C_4H_9)_4B$	20	93 dec.
VI,	$Na(C_2H_5)_3B(n\text{-}C_{12}H_{25})$	32	45 dec.

Infrared and N.m.r. Spectra.—Infrared spectra were measured with a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. Nujol mulls, Kel-F mulls, and solutions were prepared in an inert atmosphere. Ten to twenty per cent solutions of lithium tetrabutylboron, lithium triphenylbutylboron, lithium tributylphenylboron, and sodium tetraphenylboron (Matheson Coleman and Bell) in acetonitrile (spectroquality) were prepared. The lithium salts were found to follow Beer's law in the region of 2775 cm.$^{-1}$. Sodium tetraphenylboron did not absorb between 2750 and 2850 cm.$^{-1}$.

The n.m.r. absorption spectra of lithium tetrabutylboron (II) and lithium tetraethylboron (prepared from ethyllithium and triethylboron) were run as 10% solutions in acetone-d_6 (Merck, Canada) on a Varian A-60 spectrometer.

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[24] This is the basis of the double titration method of H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 286 (1954).

[25] It should be noted that the boron peroxy compound X is quite similar to the compound $(C_4H_9)_2BOOC_4H_9$ postulated as an intermediate in the air oxidation of tributylboron in tetrahydrofuran.[21] The major products from this oxidation (1-butanol, butane, and n-butyraldehyde) essentially agree with those obtained in the present study. This would indicate that intermediate X is the most likely precursor to the products observed.

[26] R. N. Meals, *J. Org. Chem.*, **9**, 211 (1944).

[27] G. Wittig, G. Keicher, A. Rüchert, and P. Raff, *Ann.*, **563**, 110 (1949).

[28] A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, and R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 3785 (1950).

Tetramethylammonium and Tetrabutylphosphonium Tetraalkylboron Compounds.—Relatively stable derivatives of sodium and lithium tetraalkylboron compounds were prepared in water solutions by reaction with tetramethylammonium or tetrabutylphosphonium bromide (the latter prepared by the method of Grayson and Keough[29] in 91% yield, m.p. 101–103°, lit.[29] m.p. 99–101°). The following derivative preparation is typical. To a solution of lithium tetrabutylboron (5.9 g., 0.024 mole) in 50 ml. of water was added a solution of 3.9 g. (0.032 mole, 33% excess) of tetramethylammonium bromide in 25 ml. of water. A white precipitate was immediately visible. The mixture was stirred for 0.5 hr., filtered, and washed until the washings showed no trace of bromide ion. The resulting solid was dried at 45° (0.1 mm.) for 1 hr. to yield 6.8 g. (91.4% yield) of tetramethylammonium tetrabutylboron, m.p. 106–112° dec. One recrystallization from ether–pentane raised the melting point to 110–112° dec. Table I summarizes our results from the preparation of stable derivatives.

Hydrolysis of Tetraalkylboron Compounds.—Hydrolysis reactions were performed in 100-ml. three-necked flask equipped with an addition funnel, magnetic stirrer, thermometer, and condenser. An outlet from the condenser led to a 100-ml. gas buret. Gases were collected at room temperature over mercury. The reaction flask was immersed in an oil bath maintained at 35 ± 1° or 60 ± 1°. Approximately 1 g. of tetraalkylboron compound was placed in a flask and allowed to equilibrate for 0.5 hr. Water, base, or acid, preheated to 35 or 60°, then was added in approximately 1 min. Zero time was taken immediately after the addition. During the reactions the volume of gas given off was recorded. After the recorded time interval (Table IV), the reaction mixture was neutralized and extracted with ether; the layers were separated. The ether layer was dried over magnesium sulfate and distilled through a 6-in. Vigreux column. After removal of the ether, tridecane was added and the distillation continued under vacuum until the head temperature reached 75° (1 mm.). The distillate was weighed and the amount of dodecane, from either III or IV, was calculated from the gas chromatographic analysis of the mixture.

The gases collected were examined by infrared and mass spectrometry and gas chromatography. Ethane and butane were separated by gas chromatography using either a silica gel column (10 ft., 60°) or an activated alumina column (Woelm, activity I, 10 ft., 70°).

No evidence for any gases except ethane or butane was obtained. Dodecane, triethylborane, and tributylborane were the only liquids isolated and identified.

Oxidation Procedure.—The following procedure for the oxidation of lithium tetrabutylboron with oxygen in tetrahydrofuran is typical.

A 500-ml. three-necked flask, equipped with a condenser, thermometer, gas inlet, and magnetic stirrer, was immersed in a constant temperature (35 ± 1°) oil bath. The outlet from the condenser led to two gas burets, one of 100-ml. capacity and the other of 500-ml. capacity. Dry tetrahydrofuran, 50 ml., was added to the flask and the apparatus, including the burets, was flushed with oxygen for 30 min. Tetrahydrofuran (25 ml.) was withdrawn and 1.0–1.5 g. of lithium tetrabutylboron dissolved in it. The solution was then introduced into the reaction flask and the system was closed to the atmosphere. Stirring was started and samples were withdrawn periodically by means of a syringe. The peroxide content was measured. No temperature rise was noted during the oxidation. A slight positive oxygen pressure (10–20 mm.) was maintained on the system and the amount of oxygen absorbed was measured by adjusting the burets. After 16 hr. argon was slowly introduced into the flask and the exit gases were passed through two Dry Ice–acetone cooled traps. Assuming all the gases except oxygen to be condensable by the traps, the amount of oxygen absorbed was calculated from the total volume decrease minus the volume of the gas in the traps. A total of 38% of the theoretical amount of oxygen was absorbed, assuming 4 moles of oxygen are required for each mole of lithium tetrabutylboron. The gas in the trap was shown to be butane by infrared and gas chromatography. A total of 15% was recovered.

The liquid layer was hydrolyzed with excess 20% sodium hydroxide solution at 60° for 2 hr. After acidification with HCl, extraction with ether, and separation of layers, the ether layer was dried with magnesium sulfate. The ether was removed by distillation and the resulting liquid was fractionated by distillation and analyzed by infrared and gas chromatography.

A 10-ft. Carbowax 20 M column at 80° was used to identify *n*-butyl alcohol (48%) and *n*-butyraldehyde (3%). The other volatile components totaled 1.4%. Only a trace amount of butyric acid remained in the distillation pot.

The oxidation of lithium tetrabutylboron was also studied in dimethylformamide and ethylene glycol dimethyl ether. Similar results were obtained.

Normal alcohols were also found to be the major products in the oxidation of lithium triethylbutylboron, lithium triethyldodecylboron, and lithium tributyldodecylboron.

Acknowledgment.—The author is indebted to Dr. C. D. Broaddus for his suggestions and stimulating discussions concerning this work. He also wishes to thank Drs. T. J. Flautt and W. L. Courchene for aid in interpreting the n.m.r. and infrared spectra and Mr. Warren Foster for patiently performing most of the work in the laboratory.

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Epoxidations with *m*-Chloroperbenzoic Acid

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Received October 7, 1963

m-Chloroperbenzoic acid is a convenient reagent for studying epoxidation reactions. When the effect of the solvent upon the rates of epoxidation of *trans*-stilbene and ethyl crotonate was examined, it was found that, with ethyl crotonate, changing the solvent had no effect on the rate of epoxidation so long as the intramolecular hydrogen bonding of the peracid was not disrupted. With one solvent, acetonitrile, an apparent zero-order reaction was observed. A scheme is proposed to account for these results.

While there have been several recent studies of epoxidations with peracids,[1-3] the only olefins examined were those that react rather readily with the peracid. Since *m*-chloroperbenzoic acid recently has become available,[4] and since solutions of this peracid are stable at moderate temperatures for prolonged periods, we were enabled to study the epoxidation of the unreactive α,β-unsaturated esters as well as *trans*-stilbene in a variety of solvents without complications due to side reactions. In all cases, blanks consisting of *m*-chloroperbenzoic acid and the solvent showed less than 2% decomposition after the epoxidation had proceeded to 50–60%. Ethyl β-methylglycidate and *trans*-stilbene epoxide were isolated in good yield from these reactions.

The second-order rate constants for the epoxidation of *trans*-stilbene with *m*-chloroperbenzoic acid at 30°

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[2] G. Berti and F. Bottari, *J. Org. Chem.*, **25**, 1286 (1960).

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