ride, 100-94-7; *n*-butyllithium, 109-72-8; *o*-(N,N-dimethylaminomethyl)diphenylmethane, 6196-39-0; N-acetyldibenzylamine, 10479-30-8.

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The Mechanism of the Oxidation of Trialkylboranes

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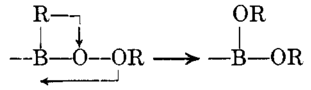
Evidence is presented to show that the air oxidation of trialkylboranes involves as one of the steps the intermolecular instead of intramolecular reaction of a boronalkyl bond with an alkylperoxyboron moiety to give two boron alkoxy groupings. This evidence was obtained from several different types of experiments. The oxidation of a trialkylborane to a borate ester can proceed through the boronate ester stage.

The following sequence of reactions has been proposed for the oxidation of trialkylboranes.[2] A similar sequence has also been presented for the autoxidation of trialkyl aluminums.[3] Equations 1 and 2 are shown

$$-\overset{|}{B}R + O_2 \longrightarrow O_2\cdot\underset{|}{\overset{|}{B}}R \longrightarrow -\overset{|}{B}O_2R \qquad (1)$$

$$-\overset{|}{B}R + -\overset{|}{B}O_2R \longrightarrow 2(-\overset{|}{B}OR) \qquad (2)$$

or



for the oxidation of one of the boron–alkyl bonds and the other two bonds may be considered oxidized or unoxidized. The formation of a complex between oxygen and the boron alkyl is followed by a rearrangement of the complex to an alkylperoxyboron compound (eq 1). In eq 2 the peroxide reacts with an unoxidized boron–alkyl bond in the same or another molecule to provide an alkoxyboron compound.

The above mechanism does not indicate if eq 2 above is inter- or intramolecular. Some workers indicate without experimental evidence that the reaction is intramolecular.[2c,d,4] If eq 2 is written as an intermolecular reaction, as the >BR (or trialkylborane) concentration increases, the peroxide concentration at any given time should decrease. An intramolecular reaction should not show this effect. This is possible because the rate of oxygen uptake (eq 1) is faster than the rate for the reaction shown by eq 2.[2,5,6] In agreement, it was recently found that lower peroxide contents occur with increasing boron alkyl concentration[5,6] and also increasing saponified alcohol yields occur with increasing boron alkyl concentration.[5] However, it was recently stated that the peroxide contents were lower at low trialkylborane concentrations.[7] The molecularity of eq 2 appears therefore to be in doubt.

Molecularity of Equation 2

If eq 2 is intermolecular, the peroxide concentration should decrease with increasing boron alkyl concentration. Our present experiments in the low trialkylborane concentration range (0.5–2.0 mole %) are in agreement with our previous results[5] in the high concentration range of 20–100 mole % and with the results of Wilke in the still lower concentration range of 0.1–0.4 mole %.[6] The reason for the discrepancy with Hansen's results,[7] discussed above, is not apparent. The solvents, temperatures, and concentrations were similar, *e.g.*, *n*-heptane *vs.* *n*-hexane solvents, 30 *vs.* 0, 20, and 65°, and the concentration range used by Hansen was 0.01–0.5 mole %.

Additional experiments have been conducted to ascertain the molecularity of eq 2. The reaction in the absence of oxygen of trialkylboranes with alkylperoxyboranes with different alkyl groups in each compound produces alcohols from the trialkylboranes as well as from the peroxyboranes upon saponification of the reaction of the reaction products. Thus, there is an oxidation of the boron alkyl by the alkylperoxyborane which would be required for an intermolecular reaction. For example, a partially air-oxidized, dilute solution of tri-*n*-butylborane in *n*-heptane was treated with a large excess of tri-*n*-hexylborane under nitrogen. The peroxide content dropped rapidly at first but then slowed down. Saponification gave a yield of *n*-hexyl alcohol corresponding to 100% of the drop in peroxide content. The same results were obtained with a more concentrated solution of tri-*n*-butylborane. A similar run was carried out with triethylborane but adding after partial oxidation only an equimolar amount of tri-*n*-butylborane. The total drop in peroxide con-

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[2] (a) T. D. Parsons, M. B. Silverman, and D. M. Ritter, *J. Am. Chem. Soc.*, **79**, 5091 (1957); (b) A. G. Davies and R. B. Moodie, *J. Chem. Soc.*, 2372 (1958); (c) M. H. Abraham and A. G. Davies, *ibid.*, 429 (1959); (d) A. G. Davies, D. G. Hare, and R. F. M. White, *ibid.*, 1040 (1960); (e) A. G. Davies, D. G. Hare, and O. R. Khan, *ibid.*, 1125 (1963); (f) N. L. Zutty and F. J. Welch, *J. Org. Chem.*, **25**, 861 (1960); (g) C. E. H. Bawn, D. Margerison, and N. M. Richardson, *Proc. Chem. Soc.*, 397 (1959).

[3] A. G. Davies and C. D. Hall, *J. Chem. Soc.*, 1192 (1963).

[4] A. G. Davies, D. G. Hare, and R. F. M. White, *ibid.*, 341 (1961); H. Hock, A. Kropf, and F. Ernst, *Angew. Chem.*, **71**, 541 (1950).

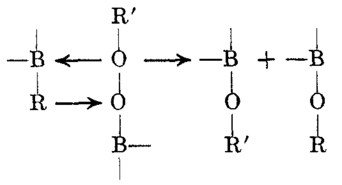
[5] S. B. Mirviss, *J. Am. Chem. Soc.*, **83**, 3051 (1961).

[6] G. Wilke and P. Heimbach, *Ann.*, **652**, 7 (1962).

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

tent was 85% instead of 100% of the original level and the yield of *n*-butyl alcohol was only 51%. These results support the intermolecular nature of step 2.

If the step (2) is intermolecular, it should most likely occur *via* transfer of an alkyl group from one molecule by boron alkyl bond scission to another molecule with attachment at a peroxide oxygen. Concomitantly, the alkoxy group from the alkylperoxy group moves to the vacated position on the other boron donating the alkyl group. The reaction may be ionic in nature since it appears to proceed faster in polar media, *e.g.*, no peroxide could be found from the beginning on of oxidation when it is carried out in the very polar media of dimethylformamide, owing to the rapid reaction of peroxide with boron alkyl. The intermolecular group transfer might also occur within a bimolecular complex (concerted mechanism) of a boron alkyl with an alkylperoxyboron compound. A radical mechanism is also possible according to the results of Hansen,[7,8] but such a mechanism[7] necessitates the formation of alkyl radicals which can lead to a variety of products. Most of these products would not give alcohol upon saponification. The high alcohol yields and lack of measurable amounts of typical radical products in reactions of alkylperoxyboron compounds with trialkylboranes in nonpolar media preclude any extensive occurrence of such a radical reaction, but do not completely eliminate it. Hansen[8] has proposed that at least two different mechanisms are operative and that one is a radical mechanism. A recent paper,[9] however, shows that radical products can arise from decomposition of the alkylperoxyboron at low temperatures instead of by interaction between trialkylboron and peroxyboron. Davies[10] suggests that a radical-chain mechanism may occur in trialkylboron autoxidation to form the alkylperoxyboron compounds by the reaction of oxygen instead of peroxyboron compounds with boron–alkyl bonds. In summary, radicals are formed in the air oxidation of alkylboron compounds, in the decomposition of alkylperoxyboron compounds, and possibly, to a limited degree, in the reaction of alkylborons with alkylperoxyborons. The only evidence for the last as a source of radicals is when either a vinyl monomer[2g,11] or iodine[7] is present.



If an intermolecular mechanism is involved, mixed or unsymmetrical borate esters should be produced when two different trialkylboranes are oxidized simultaneously. When this was tried with equimolar solutions of triethylborane and tri-*n*-propyl- or *n*-butylborane at 0–65°, only the symmetrical borate esters, triethylborate and tripropyl- or tributylborate, were found to be present by gas chromatography and no boronate esters were noted. The result was not surprising since unsymmetrical esters are spontaneously converted very rapidly to the symmetrical esters at temperatures as low as 0°.[12] Thus, the above mixtures of trialkylboranes were also oxidized at −30° in hopes of at least slowing down the conversion of mixed esters to the symmetrical ones. Much of the product was peroxidic material but there were still considerable symmetrical borate esters. A smaller but significant broad intermediate peak was present between the two symmetrical ester peaks in a gas chromatogram. It is presumed that this broad peak, not present in higher temperature oxidations, represents the unsymmetrical borate esters; there is further support for the intermolecular nature of step 2. These oxidations were carried out to the point of essentially the theoretical amount of oxygen uptake and the alcohol yields from such low temperature (−30°) runs were still moderately high (70–75%).

Mixing of two different alkyl borate esters at temperatures from −30 to +65° for several days failed to form any unsymmetrical ester and this was not a complicating concern although McCusker has indicated that with nmr such exchanges rapidly occur between borinates [$R_2B(OR)$] and boronate or borate esters at 25°.[13]

Triarylboranes are said to be more slowly oxidized than trialkylboranes because of the decrease in acidity of the boron owing to the aryl groups.[2b] The lower acidity results in a decreased tendency for borane to complex oxygen (step 1 above). It would therefore be expected that a mixture of a trialkylborane and triarylborane would give primarily oxidation of the former, but, if step 2 is intermolecular, the triarylborane might be oxidized faster than it would be alone and the trialkylborane might be oxidized slower owing to aryl group migration in competition with the alkyl group migration in eq 2.

When an equimolar solution of triphenylborane and tri-*n*-butylborane in benzene was incompletely air oxidized, the yield of phenol was double that obtained in an identical run without tri-*n*-butylborane present. The yield of *n*-butyl alcohol was a little lower than with tributylborane alone for the same oxidation time (67% instead of 75%). The results are in agreement with an intermolecular step (2). Butylbenzene was noted as a by-product in addition to the biphenyl and terphenyl; all are products of radical side reactions.

An intramolecular step (2) precludes the formation of a borinate ester (R_2BOR). Such an ester, possible in an intermolecular scheme, can be found as a reaction product.[14]

Boronate Ester Oxidation

Although it has been recently shown that all three boron–alkyl bonds can be oxidized to a borate ester,[5] it is not known if the oxidation to the borate ester proceeds *via* an intermediate boronate ester [$RB(OR)_2$] stage. It has been reported that the boronate ester is the ultimate product of the oxidation and that it is resistant to further oxidation.[2c,d,f,14] Thus, the boronate ester could not be an intermediate, and yet it is not possible to write a sequence of reactions that forms borate ester from boron alkyl, which avoids the boro-

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[8] R. L. Hansen, *J. Polymer Sci.*, **2A**, 4215 (1964).

[9] F. S. Arimoto, *ibid.*, **4A**, 275 (1966).

[10] E. C. J. Coffee and A. G. Davies, *J. Chem. Soc.*, *C*, 1493 (1966).

[11] F. J. Welch, *J. Polymer Sci.*, **61**, 243 (1962).

[12] L. H. Thomas, *J. Chem. Soc.*, 823 (1946); J. Colclough, W. Gerrard, and M. F. Lappert, *ibid.*, 907 (1955); 3006 (1956).

[13] P. A. McCusker, P. L. Pennartz, and R. C. Pilger, Jr., *J. Am. Chem. Soc.*, **84**, 4362 (1962).

[14] R. Johnson and M. G. Van Campen, Jr., *ibid.*, **60**, 121 (1938).

nate ester stage, and which still has three distinct stages of oxygen absorption. The latter is necessary according to the curve of oxygen uptake in boron alkyl oxidation.[5] The boronate ester in such a sequence of reactions could be oxidized by absorption of O_2 to form a peroxy compound (eq 3) which then is reduced to a

$$RB(OR)_2 + O_2 \longrightarrow ROOB(OR)_2 \qquad (3)$$

borate ester by intermolecular reaction with an unreacted boron–alkyl bond (eq 4). This would explain

$$ROOB(OR)_2 + -\overset{|}{B}R \longrightarrow B(OR)_3 + -\overset{|}{B}OR \qquad (4)$$

the previously found three distinct stages of oxygen absorption or two inflection points in the oxygen uptake curve and the smaller slope of the curve for each successive stage. It would be expected that R_3B would absorb oxygen faster than R_2BOX (X = OR or R) based on the decreased acidity of the latter, and certainly both should absorb much faster than $RB(OX)_2$ (eq 3) on the same basis, assuming that the boronate oxidizes.

It is also possible to go all the way to borate ester *via* the boronate ester intermediate by oxidation of the boronate by an alkylperoxyboron intermediate with a lower degree of oxidation than the peroxide in eq 4, *i.e.*

$$RB(OR)_2 + RB(OR)(O_2R) \longrightarrow B(OR)_3 + RB(OR)_2 \qquad (5)$$

$$RB(OR)_2 + R_2B(O_2R) \longrightarrow B(OR)_3 + R_2B(OR) \qquad (6)$$

However, such possibilities as reactions 5 and 6 would not allow for the three stages of oxygen uptake or two inflection points in the curve for oxygen absorption. It is possible to still satisfy this requirement if all the reactions 3–6 occur. Consequently it seems reasonable to reinvestigate whether a boronate ester can be oxidized to a borate ester.

To ascertain if reactions 3 and 4 will occur, di-*n*-butyl *n*-butylboronate was air oxidized at 65° under conditions known to give complete boron–alkyl bond oxidation with trialkylboranes (good gas–liquid contacting and high concentrations). The oxidation is very slow and after 18 hr the product gives, upon saponification, a yield of butyl alcohol corresponding to 15% of the *n*-butyl–boron bond oxidized; the yield of *n*-butylboronic acid corresponds to 20.5% oxidation. Air oxidation at 0° (optimum temperature for boron–alkyl bond oxidation[5]) after 11 hr gives 25% of the *n*-butyl–boron bond oxidized which corresponds to a total oxidation of 75% of the boron–butyl bonds in tributylborane. In good agreement tributylborane is 80% oxidized under these conditions.[5] Thus, it is possible to air oxidize boronate esters, albeit slowly and incompletely. Reactions 3 and 4 can conceivably take place, or borate esters can arise from oxidation of boron alkyls *via* the boronate ester intermediate.

Because of the somewhat faster buildup of borate ester from trialkylborane oxidation[5] than from the above boronate ester oxidations, it appears possible that reactions 5 and 6 do indeed occur simultaneously with reactions 3 and 4 in boron alkyl oxidation. The feasibility of reactions 5 and 6 has been demonstrated. Triethylborane was oxidized in dilute solution to promote a high peroxide content and then diethyl *n*-butylboronate [$C_4H_9B(OC_2H_5)_2$] was added. The peroxide content dropped slowly but considerably faster than in a control experiment where no boronate ester was added. Confirmation of the oxidation of the butyl-boron bond came in the isolation of butyl alcohol in 30% yield after saponification. The 30% butyl alcohol yield is in fair agreement with the 20% yield indicated by the drop in peroxide content. It is thus possible to oxidize a boronate ester to the borate ester by direct reaction with oxygen and/or indirectly with a peroxyboron compound.

Boron–Alkyl–Oxygen Complex

The first part of step 1 in the above mechanism is the semicomplexing of oxygen at the boron atom of the trialkylborane. Zutty and Welch have carried out supporting experiments for such a complex[2f] and Hansen has provided a theoretical basis for a transitory complex based on thermodynamic considerations of the use of oxidized boranes as polymerization catalysts.[7] Davies[2e] has not been able to repeat the experiment of Zutty and Welch. This experiment involved passing oxygen through a trialkylborane solution for a while and then sweeping out all the oxygen with nitrogen. The peroxide content markedly increased for sometime after all oxygen was removed,[2c] but Davies found a decrease in peroxide content. The peroxide increase was attributed to a relatively slow rearrangement of a more rapidly formed oxygen–borane complex. Davies postulates his lack of increase in peroxide to the absence of some unknown catalyst in the peroxide titrations of Zutty and refers to a need for a trace of ferric ion for iodometrically determining certain peroxides.[15] We have obtained substantial confirmation of this. Peroxide content increases of 25–40% were obtained with tri-*n*-butylborane in experiments similar to that of Zutty when no ferric ion was intentionally added to the iodometric titration. When a trace of ferric ion was used, only small to no increase in peroxide content occurred. Thus, a long-lived complex is not likely, but a transient "complex" is still possible.

Experimental Section

Purification of Materials.—The materials used were purified as in previous work.[3] The tri-*n*-propylborane was obtained from the Callery Chemical Co. and was redistilled before use; a heart cut was used. The triphenylborane was obtained from the Orgmet Chemical Co. and was twice recrystallized from CCl_4 under nitrogen to mp 136–138°.

Diethyl Butylboronate.—A solution of 146 g of triethylborate (1.0 mole) in 1 l. of anhydrous ether in a 5-l. flask was treated with vigorous stirring at −60 to −55° with 64 g of *n*-butyllithium (1.0 mole) as a 15 wt % solution in *n*-hexane was added dropwise over a period of 2 hr. A voluminous, white precipitate was formed. After stirring for 1 additional hr, the reaction mixture was treated with 95 g of concentrated HCl (0.97 mole) at 0° with cooling and stirring. The aqueous layer had pH 6–7. It is necessary to keep it slightly acidic or neutral to prevent hydrolysis of the ester. The layers were separated; the ether layer was dried and distilled with a 12-plate-packed column at 100 mm; a heart cut was taken at 92–96°, having a weight of 78 g (50%), $n^{20}{}_D$ 1.3987. The forerun was found to contain triethylborate and the residue contained ethyl dibutylborinate. *Anal.* Calcd for $C_8H_{19}BO_2$: C, 60.79; H, 12.11. Found: C, 61.76; H, 12.59.

When this reaction was worked up with water instead of acid, a 35% yield of butylboronic acid and an 11% yield of diethyl butylboronate were obtained. Considerable water (1.4 l.) was necessary to dissolve all of the white solid (no heat evolution), which appears to be a quite hydrolytically stable salt, $Li[B(OC_2H_5)_3C_4H_9]$.

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(15) Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

The reaction of butylboronic acid and absolute ethyl alcohol in 75% excess with benzene at reflux with a water separator gave a low yield of the desired ester. Difficulty was encountered in separation by distillation of the unreacted starting acid and the product ester, and the boroxole ester [$(C_4H_9OBO)_3$] also formed.

Dibutyl Butylboronate.—This material was prepared by heating at 120° a mixture of 181.2 g of tri-*n*-butylborane (1.0 mole) and 229 g of tri-*n*-butylborate (2.0 moles) for 5 hr with stirring. The product was distilled and an 87% yield of di-*n*-butyl-*n*-butylboronate,[16] bp 100–103° (10 mm), was obtained.

Oxidation Procedure.—The oxidations were carried out with the same equipment and in the same manner as previously.[5]

Oxidized Triethylborane plus Tri-*n*-butylborane.—The equipment described above was used, but a neck on the oxidation reaction flask was fitted with a serum cap for withdrawing samples during the run. Air was passed into a solution of 9.8 g of triethylborane (0.10 mole) in 480 g of dried *n*-heptane (0.21 mole % solution) at a flow rate of 1 l./min through a fritted glass thimble for 87 min at 0°. The total O_2 uptake corresponded to 112% oxidation to triethylborate. At this point the peroxide content corresponded to 0.438 mole/mole of B, which represents a drop from a maximum value at 62 min of 0.599 mole/mole of B. At 62 min the O_2 uptake corresponded to 100% of theory for oxidation to triethylborate. After 87 min of air flow, the flow was terminated and dry nitrogen was passed through the solution at 0° until there was less than 0.1% O_2 in the exit gas (21 min). During this 21-min period the peroxide content increased to 0.605 mole/mole of B. The nitrogen flow was continued for an additional 17 min without further change in peroxide content. A solution of 18.2 g of tri-*n*-butylborane (0.10 mole) in 25 g of dried *n*-heptane was added with stirring under nitrogen at 0°. An exothermic reaction took place and the temperature rose to 8°, and so cooling was used. In 5 min the peroxide content had dropped to 0.278 mole/mole of B, after 22 min to 0.150 mole/mole of B, and after 46 min to 0.143 mole/mole of B. The reaction mixture was allowed to stir overnight and the peroxide content had dropped to 0.096 mole/mole of B (11.2 hr elapsed time since adding tri-*n*-butylborane). The solution was then warmed to 65° and kept at this temperature for 6 hr without further change in peroxide content. After cooling, the reaction mixture, diluted with 50 ml of ether, was saponified with a solution of 10 g of sodium hydroxide (0.25 mole) in 40 g of water with external cooling to maintain the temperature at 10–15°. The aqueous layer was saturated with sodium carbonate and then extracted four times with 100 ml of ether. The combined organic layers were dried with anhydrous magnesium sulfate. All operations were carried out under nitrogen by working in a drybox. The ether was removed by distillation under nitrogen with a 10-plate Oldershaw column at a 3:1 reflux ratio. The butyl alcohol content of the residue was determined by gas chromatography and corresponded to 51 mole % yield based on the total drop in peroxide content (0.485 mole/mole of B).

Oxidized Tri-*n*-butylborane plus Tri-*n*-hexylborane. Part A.—This reaction was carried out similar to the above except that 4.90 g of tri-*n*-butylborane (0.025 mole) in 495 g of *n*-heptane (0.05 mole % solution) was air oxidized at 0° to a peroxide content of 0.70 mole peroxide/mole of boron, which took 21 min. The peroxide content increased to 0.76 mole/mole of B during the next 35 min, while nitrogen was now passed through the solution. All oxygen was out of the system by a 36-min total elapsed time, but there was a slight increase in peroxide content until a 56-min total elapsed time and then the peroxide content remained constant at 0.81 mole/mole of B for 26 additional min. A solution of 26.6 g of tri-*n*-hexylborane (0.10 mole) in 50 ml of *n*-heptane was added with stirring at 0° and in 2.5 min the peroxide had dropped to 0.24 mole/mole of B and in 1 hr it had dropped to 0.04 mole/mole of B. The reaction mixture was allowed to stand overnight at 25° and then saponified as above at 25° with 30 g of 50% sodium hydroxide diluted with 85 g of water. The *n*-hexyl alcohol content of the distillation residue (2.0 g) corresponded to the total decrease in peroxide content (0.77 mole/mole of B).

Part B.—The same reaction was now carried out for the air oxidation of 18.2 g of tri-*n*-butylborane (0.10 mole) in 482 g of *n*-heptane (0.21 mole % solution) at 0°. The air was turned off after 80 min and the peroxide content was 0.445 mole/mole of B. The oxygen uptake corresponded to 106% of theory for oxidation to tributylborate. The peroxide content dropped to 0.420 mole/mole of B over the next 20 min, while nitrogen bubbled through the solution. $FeCl_3$ was used in this experiment for the iodometric titrations for peroxide content. A solution of 79.8 g of tri-*n*-hexylborane (0.30 mole) in 50 ml was added and the peroxide dropped to nil in 5 min. Saponification and work-up as above gave a yield of *n*-hexyl alcohol (4.8 g) corresponding to the drop in peroxide content.

Air Oxidation of Mixed Trialkylborons.—A solution of 24.5 g of triethylborane (0.25 mole) and 35.0 g of tripropylborane (0.25 mole) in 59.5 g of *n*-heptane was air oxidized as above at 65° until there was no further O_2 uptake (11 hr) and the total O_2 absorption amounted to 87% of theory for oxidation to the borate esters. A gas chromatographic scan of the product solution with a 2-ft 5% silicone gum rubber column with an F & M 500 gas chromatographic unit with column temperatures of 50–175° showed strong peaks for triethyl and tripropylborates, but nothing between. Gas chromatograms of mixtures of these two esters stirred for 6–14 hr with and without *n*-heptane diluent at −30 to +65° showed peaks for only the two original symmetrical esters. The oxidation product was saponified with a solution of 25 g of sodium hydroxide in 100 g of water at 10–25° and worked up as before. The yield of ethanol was 88 mole % and the yield of *n*-propyl alcohol was 70%.

The same gas chromatographic results were obtained in an identical run made at 0°. When the oxidation was carried out at −30° the gas chromatograph (column temperature 50°, the minimum useful temperature) showed a broad peak intermediate between the symmetrical ester peaks. This broad peak could not be resolved into separate peaks by using other column packings, etc. Allowing the oxidation product to stand for 24 hr at room temperature caused the intermediate peak in the gas chromatogram to disappear. The total oxygen uptake at the point of essentially no further oxygen absorption was 99% of theory. Saponification of the oxidation product gave a 71% yield of ethanol and a 74% yield of *n*-propyl alcohol.

An otherwise identical oxidation made with tri-*n*-butylborane in place of tripropylborane at 0° gave the same results as above at this temperature. Alcohol yields were 87% for ethanol and 71% for *n*-butyl alcohol. This same run at −30° gave the same chromatographic results as in the above −30° oxidation. The alcohol yields were 71% for ethanol and 75% for *n*-butyl alcohol.

Oxidation of Triphenylborane.—A solution of 48.4 g of triphenylborane (0.20 mole) in 194 g of dry benzene (8.3 mole % solution) was air oxidized at 55–60° for 120 min, but essentially all of the oxygen absorption occurred during the first 60 min. The total oxygen absorption was equivalent to 33% oxidation. The reaction mixture was saponified at 25° with a solution of 26 g of NaOH in 234 g of water. Gas chromatographic analysis of the product showed yields of 2.6 g of phenol (4.6% on triphenylborane and 13.8% on oxygen uptake), 7.4 g of biphenyl (16.1% on triphenylborane and 48.3% on oxygen uptake), and 1.6 g of terphenyl (3.5% on triphenylborane and 10.5% on oxygen uptake). The total yield of phenyl groups for the three products was 83.7% assuming that one bond oxidized.

Oxidation of Triphenylborane and Tri-*n*-butylborane.—A mixture of 36.4 g of tri-*n*-butylborane (0.20 mole) and 48.4 g of triphenylborane (0.20 mole) in 194 g of benzene was air oxidized for 130 min at 60°. There was still a significant oxygen absorption at this point and the total oxygen uptake corresponded to 98% oxidation of one of the boranes. Saponification with 48 g of sodium hydroxide in 350 ml of water at 25° produced (according to gas chromatography) 4.6 g of phenol (9% yield), 30.0 g of *n*-butyl alcohol (67% yield), 3.7 g of biphenyl (8% yield), 2.8 g of terphenyl (6% yield), and a very small amount of butylbenzene. The total yield of phenyl groups for the three products was 69%, assuming that one bond oxidized in triphenylborane.

Oxidation of *n*-Butyl *n*-Butylboronate.—A solution of 107 g of *n*-butyl *n*-butylboronate [$C_4H_9B(OC_4H_9)_2$, 0.50 mole] in 107 g of *n*-heptane (50 wt % solution) was air oxidized as above at 65° for 18 hr with almost no uptake of oxygen during the last 10–12 hr. The total O_2 uptake amounted to 39% oxidation of the *n*-butyl–boron bond. The product was saponified with a solution of 65 g of NaOH in 260 g of water at 20–30° with cooling. It was necessary to add an additional 150 g of water during ether extraction of the saponification reaction mixture to prevent extraction of the sodium butylboronate by the ether. The ether was removed from the combined organic layer and ether washings

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(16) H. I. Schlesinger, H. C. Brown, D. L. Mayfield, and J. R. Gilbreath, *J. Am. Chem. Soc.*, **75**, 213 (1953); J. Furukawa, T. Tsuruta, T. Imada, and H. Fukutani, *Makromol. Chem.*, 122 (1959).

by distillation and the residue was found by gas chromatography to contain 79.5 g of *n*-butyl alcohol for a 15% yield based on butyl-boron bond, assuming a 100% yield of butyl alcohol from the two butoxy groups. Hence, the 15% yield is a minimum figure. The aqueous layer after ether extraction was acidified and the butylboronic acid was suction filtered and allowed to air dry. It had a weight of 40.5 g [mp 83–85° and, with pure material of mp 92° (Callery Chemical Co.), mmp 90–92°] for a 79.5% yield or 20.5% oxidation of the butyl-boron bond. On this basis the total butyl alcohol yield was 73%.

The above run was repeated at 0° for 11 hr and the butyl alcohol weight was 83.0 g for a 24.5% minimum yield assuming a 100% yield of butyl alcohol from the two butoxy groups. The total butyl alcohol yield was 74.9%.

Oxidation of Diethyl *n*-Butylboronate with Oxidized Triethylborane.—A solution of 10.0 g of triethylborane (0.10 mole) in 480 g of *n*-heptane was air oxidized as above at 0° for 82 min. The peroxide content at this point had reached 0.457 mole/mole of B. The air was shut off and nitrogen was passed through until there was no further oxygen in the exit gas (<0.1% oxygen). A solution of 47.4 g of diethyl *n*-butylboronate (0.30 mole) in 50 g of *n*-heptane was added at 0° with stirring. The reaction mixture was slowly heated to 50° during 1 hr (peroxide content now 0.390 mole/mole of B) and then kept at 50° for 13 hr. The peroxide content had dropped to 0.254 mole of peroxide/mole of B for a total drop of 45% and 42% of this drop occurred during the first hour. The drop in peroxide content corresponds to about a 20 mole % yield of *n*-butyl alcohol from the diethyl *n*-butylboronate. After saponification of the oxidation reaction product, a yield of 2.2 g of butyl alcohol was found which corresponds to a 30 mole % yield based on the boronate ester.

Registry No.—Triethylborane, 97-94-0; tri-*n*-butylborane, 122-56-5; tri-*n*-hexylborane, 1188-92-7; tripropylborane, 1116-61-6; triphenylborane, 960-71-4; diethyl butylboronate, 10394-51-1; dibutyl butylboronate, 3027-58-5.

Preparation and Reactions of Some Alkylthiomethyllithium Compounds

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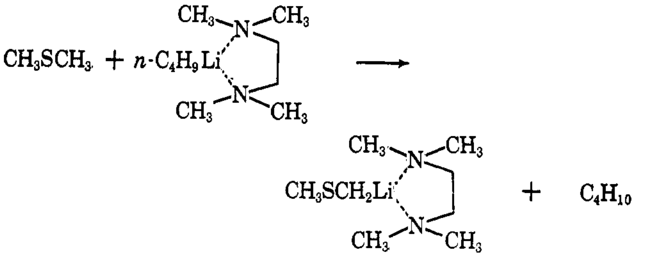
The highly reactive complex comprised of *n*-butyllithium and N,N,N′,N′-tetramethylethylenediamine readily metalates dimethyl sulfide to give high yields of methylthiomethyllithium. The thiomethyllithium compound has been shown to be of value as an intermediate in the synthesis of carbon functionally substituted sulfides by its reactions to give $C_6H_5CH(OH)CH_2SCH_3$, $n\text{-}C_3H_7CH(OH)CH_2SCH_3$, $(CH_3)_3SiCH_2SCH_3$, $(C_6H_5)_2PCH_2SCH_3$, $P(CH_2SCH_3)_3$, and $CH_3SC_{11}H_{23}$. The reaction of the metalating complex with dialkyl sulfides containing β hydrogens resulted primarily in the formation of olefins.

As part of an extensive study of the reactions of organometallic compounds with weak organic acids, Gilman and co-workers, several years ago, investigated the reaction of *n*-butyllithium with methyl phenyl sulfide and ethyl phenyl sulfide in diethyl ether.[1] They established that, in contrast to methyl phenyl sulfide which underwent lateral metalation, ethyl phenyl sulfide was metalated on the aromatic ring to give *o*-lithiophenyl ethyl sulfide. Very recently, Corey and Seebach reported[2] a greatly improved procedure for the preparation of phenylthiomethyllithium which utilized *n*-butyllithium complexed with diazabicyclo[2.2.2]octane as the metalating agent.

Surprisingly, no systematic attempt appears to have been made to extend the metalation of sulfur compounds to include the less reactive dialkyl sulfides. In view of the current interest in and widespread utilization of other sulfur-stabilized carbanions such as $R_2S^+CH_2^-$, $CH_3S(O)CH_2M$, and $R_2S^+(O)CH_2^-$, we have independently developed a method for the preparation of some alkylthiomethyllithium compounds[3] which parallels to some extent the method reported by Corey and Seebach for the preparation of phenylthiomethyllithium. Our method is particularly useful for the preparation of the parent compound, methylthiomethyllithium, CH_3SCH_2Li (I).

Results

Methylthiomethyllithium is readily obtained from the reaction of dimethyl sulfide with the potent metalating complex[4] comprised of equimolar quantities of *n*-butyllithium and N,N,N′,N′-tetramethylethylenediamine (TMEDA). The reaction is quite rapid at room temperature (essentially complete within 4 hr) and in hexane solvent, thereby obviating the necessity for using organometallic-sensitive ethers.[5]



Compound I has been characterized by H[1] nmr spectral analysis and by chemical derivatization with several reagents.

An H[1] nmr spectrum obtained on a benzene solution of I had signals centered at τ 7.92 (relative to benzene) for the methyl protons and 9.26 for the methylene protons. This corresponds to an internal chemical shift of 1.34 ppm which is somewhat smaller than that found for the related trimethylsilylmethyllithium compound.[6] The TMEDA portion of the complex was

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(1) (a) H. Gilman and F. J. Webb, *J. Am. Chem. Soc.*, **71**, 4062 (1949). (b) For a comprehensive review of metalation reactions, see H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 258 (1954).

(2) E. J. Corey and D. Seebach, *J. Org. Chem.*, **31**, 4097 (1966).

(3) The literature contains two reports describing attempted preparations of alkylthioalkylmetal compounds by nonmetalation routes: F. G. Bordwell and B. M. Pitt [*J. Am. Chem. Soc.*, **77**, 572 (1955)] were unsuccessful in their efforts to prepare CH_3SCH_2MgCl from chloromethyl methyl sulfide, and W. E. Parham, M. A. Kalnins, and D. R. Theissen [*J. Org. Chem.*, **27**, 2698 (1962)] met with limited success (*ca.* 5% yields) in the preparation of α-lithioalkyl hexyl sulfide by additions of organolithium compounds to *n*-hexyl vinyl sulfide.

(4) (a) G. G. Eberhardt and W. A. Butte, *ibid.*, **29**, 2928 (1964); (b) A. W. Langer, Jr., *Trans. N. Y. Acad. Sci., Ser. II*, **27**, 741 (1965); (c) D. J. Peterson, *J. Organometal. Chem.*, in press.

(5) See, for example, C. D. Broaddus, *J. Org. Chem.*, **30**, 4131 (1965), and references cited therein.

(6) G. E. Hartwell and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4625 (1966); J. W. Connolly and G. Urry, *norg. Chem.*, **2**, 645 (1963).