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REACTION OF ALKALI METAL DIBUTYLBORON WITH ALKYL HALIDES IN DIETHYL ETHER SOLUTION*

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SUMMARY

The reaction of alkali metal dibutylboron (I), prepared by the treatment of dibutylchloroborane with sodium/potassium alloy in diethyl ether, with alkyl iodides has been studied. Very little alkylation on boron to produce dibutylalkylborane occurs in ether solution at room temperature. The alkyl iodide reacts to produce mainly alkane and alkyl dimer. The reaction is believed to occur by electron transfer from (I) to RI followed by decomposition of the $RI^{\overline{\cdot}}$ to iodide ion and alkyl radical.

Kraus and Auten[2] described the formation of alkali metal dibutylboron*** (I) dibutylchloroborane with potassium/sodium alloy in ether. They reported that (I) reacted with methyl iodide to form dibutylmethylborane in 45% yield. Reaction of (I) with dibutylchloroborane resulted in the formation of tributylborane and a difficultly volatile substance corresponding in analysis to "dibutylboron".

$$(C_4H_9)_2BCl + K/Na \xrightarrow[\text{ether}]{} \underset{\text{(I)}}{(C_4H_9)_2BM} + MCl \xrightarrow{CH_3I} (C_4H_9)_2BCH_3 \qquad (M = Na \text{ and/or } K)$$

More recently Köster and coworkers[6] reported that the reaction of dibutylchloroborane with alkali metals produced the dialkylboryl radical (II) which underwent hydrogen atom migration followed by reaction with a second diethylboryl radical to produce (III). The solvent employed in the reaction was not specified, although Köster states that (II) can be formed and trapped by reaction with pyridine, quinoline, and isoquinoline in ether or tetrahydrofuran. (Unfortunately, the experi-

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* Part XXIV of Transfer Reactions Involving Boron. For part XXIII see ref. 1. Submitted by P. W. W. in partial fulfillment of the requirements for the Ph.D., University of Notre Dame, 1971.

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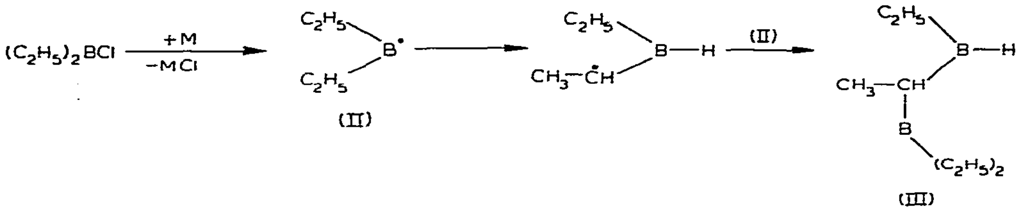
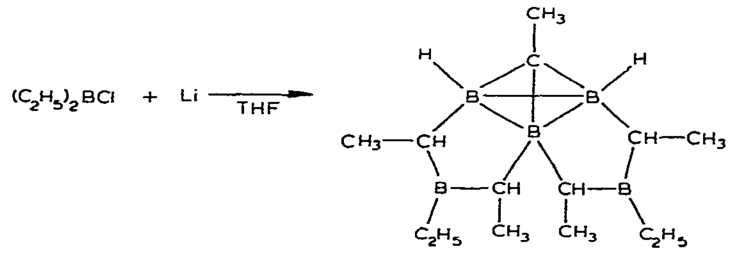
*** The identity of the alkali metal associated with the dibutylboryl group has not been rigorously identified. Parsons and coworkers[3,4] have referred to the compound as the potassio derivative.

The reaction product from tri-n-butylborane with sodium/potassium alloy has been referred to as potassium di-n-butylborate[3,4] and alkali metal di-n-butylboron[2]. As the recently adopted rules on the nomenclature of boron compounds[5] do not provide nomenclature rules for such compounds, we are arbitrarily using the designation alkali metal di-n-butylboron.



mental details and structural information were not given). In a companion article Köster and Benedikt[7] report that the reaction of equimolar quantities of diethylchloroborane and lithium in tetrahydrofuran led, in part, to the formation of the carborane (IV). Interestingly, when tetraethyldiborane is "simmered" with metallic



(IV)

sodium, (IV) is also formed[8] (The structure of (IV) was assigned by analysis of the ^{11}B NMR and mass spectrum of the compound).

Parsons and coworkers[3,4] have reported that (I) reacts with trifluoroiodomethane in triethylamine solution to produce dibutyl(trifluoromethyl)borane. These authors reported that small amounts of tributylborane, hydrogen, butene and trifluoromethane were also formed. These authors indicated that the use of diethyl ether as solvent led to complications; however, the nature of the complications was not discussed.

$$(I) + CF_3I \rightarrow F_3CB(C_4H_9)_2$$

Our interest in attempting to introduce a dialkylboryl group into an organic substrate led us to investigate the chemistry of alkali metal dibutylboron as a potential nucleophilic reagent. Our results differ substantially from those reported earlier and provide an insight into the unusual chemistry associated with (I). Dibutylchloroborane was allowed to react with two equivalents of potassium/sodium alloy in diethyl ether at room temperature. After completion of the reaction the solids were precipitated by centrifugation leaving a clear dark brown solution. The ^{11}B NMR spectrum displayed a relatively weak signal at 15 ppm (relative to boron trifluoride etherate internal capillary) superposed on a very broad peak. Direct analysis of the solution by GLC showed the presence of tributylborane (~10% yield)*. An aliquot of the sample

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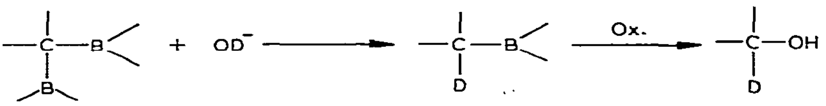
* The reaction of chlorodiphenylborane with sodium/potassium alloy in dimethoxyethane has been reported to yield triphenylborane which undergoes further reduction to produce triphenylborane radical anion[9].

was hydrolyzed with sodium deuteroxide in deuterium oxide and followed by oxidation with basic hydrogen peroxide. The 1-butanol was isolated and analyzed by mass spectrometry and shown to contain only normal 1-butanol. This observation precludes the formation of species such as (III) with two boron atoms attached to a single carbon atom under the present conditions[10]. Species containing a B–H



capable of undergoing hydroboration of an olefin [as should (III)] were shown not to be present in the reaction mixture or formed during the reaction of (I) with methyl iodide by the lack of formation of 1-hexanol after addition of 1-hexene followed by hydrolysis and oxidation.

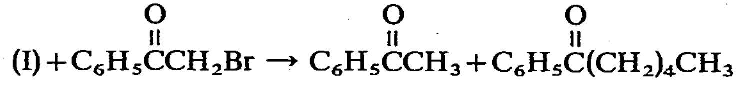
The addition of methyl iodide to an ether solution of (I) at room temperature resulted in a vigorous exothermic reaction accompanied by gas evolution and formation of a white precipitate. The evolved gas was analyzed by mass spectrometry and shown to contain methane and ethane in a 7/1 ratio (the absolute yield was not determined). Direct analysis of the reaction mixture by GLC showed the presence of tributylborane (13%) and less than 1% of dibutylmethylborane. (Dibutylmethylborane was prepared by treating dibutylchloroborane with methyl lithium in ether at −78° followed by immediate GLC analysis and comparison of retention times). Hydrolysis of the reaction mixture followed by basic oxidation produced 1-butanol and a trace of methanol.

Similar results were obtained from reactions of other alkyl iodides with (I). The reaction of (I) with n-heptyl iodide was considerably slower. Direct analysis of the reaction mixture after 24 h showed the presence of tributylborane (9%), n-heptane (24%) and small quantities (< 1%) of n-octane, n-undecane, and n-tetradecane. Hydrolysis followed by basic oxidation produced 3% of 1-heptanol.

$$\text{(I)}+C_7H_{15}I \rightarrow \underset{3\%}{(C_4H_9)_2BC_7H_{15}}+\underset{24\%}{C_7H_{16}}+\underset{<1\%}{C_8H_{18}}+\underset{<1\%}{C_{11}H_{24}}+\underset{<1\%}{C_{14}H_{30}}$$

Treatment of (I) with benzyl bromide led to a fairly rapid reaction and produced toluene (30%) and bibenzyl (2%). No n-pentylbenzene was detected. Hydrolysis followed by basic oxidation did not produce any benzyl alcohol.

Finally, reaction of (I) with phenacyl bromide led to the formation (before hydrolysis) of acetophenone (15%) and caprophenone (2%).



$$\text{(I)}+C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}CH_2Br \rightarrow C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}CH_3+C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_4CH_3$$

Alkyl bromides and chlorides react exceedingly slowly with (I), and the reactions were not studied in detail.

The results given above are consistent with an electron transfer from (I) to the organic halide followed by loss of halide ion and formation of an alkyl radical.

The alkyl radical abstracts a hydrogen atom (from an undetermined source) to produce alkane, or undergoes dimerization to form the alkyl dimer. The alkyl radical also appears to react with the tributylborane present in the reaction mixture to displace an n-butyl radical similar to the displacement of a methyl radical from trimethylborane by tert-butoxy radical as reported by Kochi and Krusic[11]. The butyl radicals thus formed react to form butane (not analyzed for), and dimerization products with the other radicals in solution.

$$(C_4H_9)_2BM+RI \longrightarrow (C_4H_9)_2B^{\bullet}+\begin{array}[t]{c}RI^{\bar{\bullet}}\\ \downarrow \\ R^{\bullet}+I^-\end{array}+M^+$$

$$R^{\bullet}+R'H \longrightarrow R'^{\bullet}+RH \quad \text{(R}' \text{ of undetermined structure)}$$

$$2\,R^{\bullet} \longrightarrow R\text{–}R$$

$$R^{\bullet}+(C_4H_9)_3B \longrightarrow RB(C_4H_9)_2+C_4H_9^{\bullet}$$

$$R^{\bullet}+C_4H_9^{\bullet} \longrightarrow C_4H_9\text{–}R$$

The mechanism of formation of the alkyldi-n-butylborane cannot be uniquely specified. It is possible that the alkyl and di-n-alkylboryl radicals combine; the yield

$$R^{\bullet}+(C_4H_9)_2B^{\bullet} \longrightarrow R\text{–}B(C_4H_9)_2$$

of alkyldi-n-butylborane being roughly the same as for the formation of the other alkyl radical dimerization products. Alternatively, the alkyldi-n-butylborane may be formed in a direct nucleophilic displacement reaction.

Attempts were made to determine the ultimate fate of the dibutylboryl radical by physical and chemical means. The solvent and the more volatile hydrocarbon products were removed under reduced pressure and the resulting residue was analyzed by mass spectrometry. Low temperature mass spectra ($< 150°$) of the residues (direct injection probe) were typical of tributylborane[12] in the higher mass region (> 100 *m/e*). Increasing the probe temperature to $> 175°$ resulted in the appearance of series of peaks in the 220, 230, and 250 *m/e* region corresponding to species containing three, four, and five boron atoms, respectively, as determined from the relative peak intensities within each series of peaks. These series of peaks appear in the same region as those reported for the carboranes [including (IV)] reported by Köster in the reaction of diethylchloroborane with lithium in THF. However, it has been discovered that tributylborane undergoes rapid thermal decomposition ($t_{\frac{1}{2}} < 10$ min) in the mass spectrometer at pressures below 2×10^{-6} mm and temperatures above 175° [12], and we feel that the series of peaks observed in the high temperature mass spectra of our samples are due to the thermal decomposition of the tributylborane present in the sample, and not to the carboranes that might have been formed earlier in the reaction*. At the present time we have no evidence for or against the presence of carboranes such as (IV) in the reaction residues.

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* It is interesting to note that the same *m/e* series of peaks are obtained from diethylchloroborane and tributylborane. This is under further study.

Oxidation with basic hydrogen peroxide of the final reaction mixtures, before removal of the volatile products, gave a total recovery of the butyl groups, as 1-butanol, of 95% thus precluding unusual compound formation as reported by previous investigators[6,7]. The dibutylboryl radical does not abstract a hydrogen to form dibutylborane as evidenced by the lack of hydroboration of 1-hexene added to the solution of (I) prior to the addition of the alkyl halide. The quantity of tributylborane present after the reaction of (I) with the alkyl halides is only very slightly increased over the amount present before reaction, the increase in tributylborane not being substantial enough to account for the required disappearance of the dibutylboryl radicals.

The ^{11}B NMR spectra of the reaction product mixtures displayed peaks at -88 (trialkylborane) and -52 ppm (dialkylborinate). It would appear that the dibutylboryl radical, or some other reactive species in the reaction mixture, is reacting with the solvent diethyl ether leading to as yet unidentified dibutylborinate derivatives. This is not unexpected in that the alkali metal dibutylboron is probably intimately solvated or complexed with one or more molecules of diethyl ether. This could well be the reason for the apparent difference in reactivity between (I) in ether, hydrocarbon, and triethylamine solution.

EXPERIMENTAL

Preparation of alkali metal dibutylboron (I)

Sodium/potassium alloy was prepared according to the method of Kraus and Auten[2]. The alloy (1.37 g, 27.4 mmol of potassium metal) was placed in a dry three-necked flask fitted with an addition funnel, reflux condenser, nitrogen atmosphere inlet, and magnetic stirrer. Diethyl ether (20 ml) was added and 2.18 g (13.5 mmol) of di-n-butylchloroborane was added dropwise with rapid stirring. After completion of the addition of the dibutylchloroborane the reaction mixture was stirred vigorously for 12 h. The addition funnel was replaced by a rubber septum and the entire reaction mixture was transferred by syringe to a dry, nitrogen filled centrifuge tube fitted with a rubber septum. The reaction mixture was centrifuged and the clear brown supernatant was removed by syringe and stored in a sealed vessel under a nitrogen atmosphere.

The ^{11}B NMR spectrum of the solution displayed a signal at 15 ppm (relative to boron trifluoride internal capillary) superposed on a very broad peak near 0 ppm. Direct analysis of the ethereal solution of (I) by GLC on a 6 ft Silicone oil DC-550 on Diatoport W column at 100° (injector temperature 100°) using tert-butylbenzene as an internal standard showed the presence of an average 9% tributylborane.

Reaction of (I) with methyl iodide

To a solution of (I) prepared from 4.6 mmol of dibutylchloroborane was added dropwise 0.66 g (4.7 mmol) of methyl iodide. A vigorous reaction ensued with evolution of gas and formation of a copious white precipitate. A sample of the evolved gas was analyzed by low voltage, high-resolution mass spectrometry showing the presence of methane at m/e 16.032 (calcd.: m/e 16.031) and ethane at m/e 30.043 (calcd.: m/e 30.047) in a ratio of 7/1.

The precipitate was allowed to settle and the ^{11}B NMR spectrum of an aliquot of the reaction mixture was recorded showing peaks at -88 and -52 ppm in an 8/1 intensity ratio. Direct analysis of the reaction mixture by GLC on a 6 ft 10% Silicone oil DC-550 on Diatoport W column at 100° (injector temperature 100°) using tert-butylbenzene as an internal standard showed the presence of tributylborane (13%) and dibutylmethylborane (< 1%).

Preparation of di-n-butylmethylborane

Dibutylchloroborane (1.60 g, 10 mmol) in diethyl ether was reacted with 4.37 ml of 2.06 *M* (9 mmol) methyl lithium in ether at −78°. The reaction mixture was allowed to come to room temperature and was immediately analyzed by GLC on a 6 ft 10% Silicone oil DC-550 on Diatoport W column at 130° (injector temperature 108°) showing the presence of a single volatile product (no tributylborane was present).

An aliquot of the reaction mixture was oxidized with *m*-chloroperbenzoic acid producing 1-butanol and methanol as indicated by GLC analysis on a 6 ft Carbowax 20 *M* on Chromosorb W column.

Reaction of methyl iodide with (I) in the presence of 1-*hexene*

Methyl iodide (0.63 g, 4.4 mmol) and (I) (from 4.4 mmol of dibutylchloroborane) were reacted as described above in the presence of 0.38 g (4.4 mmol) of 1-hexene. After the reaction was complete the reaction mixture was cooled in an ice bath and sodium hydroxide (1 ml of 3 *N*) and hydrogen peroxide (1 ml of 30%) were added. The reaction mixture was stirred for 30 min and was extracted with ether. Analysis of the ether extract by GLC on a 27 ft Carbowax 20 M column showed the complete absence of 1-hexanol.

Deuterolysis of the reaction mixture of (I) with methyl iodide

A reaction mixture derived from 1.42 g (10 mmol) of methyl iodide with (I) (from 10 mmol of dibutylchloroborane) was treated with sodium deuteroxide in deuterium oxide (prepared by the dissolution of 0.46 g (20 mmol) of sodium in 6.5 ml of deuterium oxide) and stirred for 12 h at room temperature. The reaction mixture was cooled to 0° and 3 ml of 30% hydrogen peroxide were added. The mixture was stirred for one h, saturated with potassium carbonate, and was extracted with ether. The solvent was removed and the 1-butanol was purified by preparative GLC on a Carbowax 20 M on Chromosorb W column. The infrared spectrum of the 1-butanol showed no C–D stretching absorption, and the mass spectrum was identical in all respects with pure 1-butanol.

Reaction of n-heptyl iodide with (I)

n-Heptyl iodide (2.06 g, 9.1 mmol) was added to an ethereal solution of (I) prepared as described above from 9.1 mmol of dibutylchloroborane. The reaction was stirred at room temperature for 60 min and was directly analyzed by GLC using a 6 ft 10% Silicone oil DC-550 on Diatoport column at 100° (injector temperature 100°) using tert-butylbenzene as an internal standard showing the presence of 10% tributylborane. After 24 h GLC analysis on a 12 ft 20% Carbowax 20 M on Chromosorb W column showed the presence of n-heptyl iodide, n-heptane (24%) with small quantities (< 1%) of n-octane, n-undecane, and n-tetradecane by comparison of retention times with authentic materials.

The reaction mixture was cooled to 0° and 4.7 g (27.3 mmol) of *m*-chloroperbenzoic acid was slowly added. The reaction mixture was stirred for several hours at room temperature, and was analyzed directly by GLC on a 6 ft 20% Carbowax 20 M on Chromosorb W column showing the presence of 1-butanol (95%) and 1-heptanol (3%).

Reaction of benzyl bromide with (I)

The addition of 0.82 g (4.8 mmol) of benzyl bromide to (I) prepared as described above from 4.8 mmol of dibutylchloroborane produced immediate formation of a white precipitate. The precipitate was allowed to settle and the ^{11}B NMR spectrum of the reaction solution was recorded showing the presence of peaks at -88 and -52 ppm. Direct analysis of the reaction mixture by GLC on a 12 ft 20% Carbowax 20 M on Chromosorb W column using ethylbenzene and eicosane as internal standards showed the presence of toluene (30%) and dibenzyl (2%). No amylbenzene was found.

Oxidation of the reaction mixture with basic hydrogen peroxide at 0° produced 1-butanol, but no benzyl alcohol. The yield of toluene (due to possible base-catalyzed hydrolysis of the B–benzyl carbon bond) did not increase on treatment with the basic hydrogen peroxide.

Reaction of phenacyl bromide with (I)

The addition of 1.44 g (7.25 mmol) of phenacyl bromide to an ethereal solution of (I) prepared as described above from 7.25 mmol of dibutylchloroborane resulted in the immediate formation of a white precipitate. The precipitate was allowed to settle and the ^{11}B NMR spectrum of the reaction mixture was recorded showing the presence of peaks at -88 and -53 ppm. Direct analysis of the reaction mixture by GLC on a 29 ft 20% FFAP on Chromosorb W column showed the presence of acetophenone (15%) and caprophenone (2%).

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