A New Convenient Preparation of Dialkylbromoboranes

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Summary Dialkyl(methylthio)boranes react rapidly with bromine at low temperatures in a redox reaction that gives pure dialkylbromoboranes in high yield.

ALTHOUGH dialkylhalogenoboranes have great potential as intermediates in the synthesis of other classes of boron compounds[1] as well as in organic synthesis,[2] the problems of preparing them in a pure state in high yield have left this potential largely unfulfilled. The reaction of anhydrous HCl with trialkylboranes at elevated temperatures[3] and the introduction of chloroborane in diethyl ether as a hydroborating agent[4] to some extent overcome these obstacles for chloroboranes, but bromoboranes remain difficult to prepare. Thus, the reported procedure to convert tri-n-butylborane into di-n-butylbromoborane by reaction with hydrogen bromide proceeds with a low conversion and is a tedious and difficult procedure.[5] Organometallic reagents may react with tribromoborane to give the desired products[1] but once again isolation procedures are difficult, dismutations may occur, and valuable groups may be lost.[1,6] Thus the chemistry of dialkylbromoboranes is little known.

The radical reaction of a thiol with a trialkylborane proceeds in mild conditions in good yield to give a dialkyl(alkylthio)borane (I), the only by-product being an alkane which may be readily removed if desired.[7] We now report that compounds (I) react practically instantaneously at -63 °C with bromine according to equation (1), to give the dialkylbromoborane (II) and a disulphide (III). The reaction is general, but for preparative purposes it is convenient to have $R^2 = Me$ so that the product disulphide is volatile and readily removed *in vacuo* to leave substantially pure (II).

$$\underset{(I)}{2R^1_2BSR^2} + Br_2 \longrightarrow \underset{(II)}{2R^1_2BBr} + \underset{(III)}{R^2SSR^2} \qquad (1)$$

TABLE

R^1 in $R^1_2BSR^2$	Yield[a] of R^1_2BBr(%)
n-Butyl	90
n-Pentyl	98
n-Hexyl	97
n-Octyl	96
Cyclopentyl	82
Cyclohexyl	86
2-Methylcyclohexyl . .	78

[a] All compounds were characterised by bromine analysis and conversion into the corresponding borinic acid or methyl borinate, which gave satisfactory analyses or were compared directly with authentic samples.

The Table gives yields of distilled products obtained by application of this procedure to representative dialkyl(methylthio)boranes. The yields are essentially quantitative for primary alkyl groups and only a little lower for secondary alkyl groups, where some α-bromination may occur.[8] Well defined dialkylbromoboranes thus become readily available for the first time. We are exploring the chemistry of these compounds and have already shown how they may be used in a versatile synthesis of mixed trialkylboranes.[9]

It is most interesting to note that the redox reaction described proceeds in exactly the opposite sense to the one between dialkyliodoboranes and disulphides which gives iodine and dialkyl(alkylthio)boranes.[10] Clearly such well defined redox reactions have great scope in the preparation of various substituted organoboranes.

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