The Photochemically Induced Reaction of Bromotrichloromethane with Triethylborane and Related Trialkylboranes. A New Route to α-Bromination of Trialkylboranes

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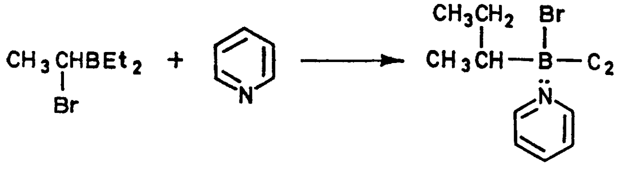
Summary Bromotrichloromethane undergoes a photochemically induced reaction with triethylborane and related trialkylboranes to produce chloroform and the corresponding α-bromotrialkylborane; the reaction provides a method for producing the reactive α-bromoorganoborane without the simultaneous production of destructive hydrogen bromide.

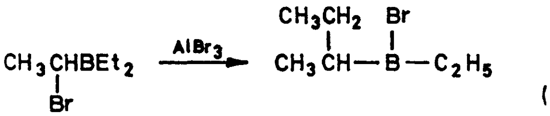
The photochemical bromination of organoboranes with elemental bromine results in the selective substitution of the α-position (Equation 1).[1,2]

$$\mathrm{CH_3CH_2BEt_2 + Br_2 \xrightarrow{h\nu} CH_3{\cdot}CHBr{\cdot}BEt_2 + HBr} \qquad (1)$$

These α-bromo-derivatives are of considerable theoretical and practical interest. For example, they undergo remarkably easy rearrangement under the influence of nucleophilic[2] and electrophilic[3] catalysts (Equations 2, 3).



(2)

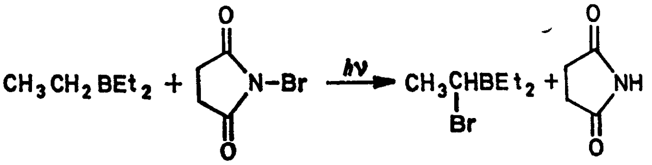


$$\mathrm{CH_3\underset{Br}{C}HBEt_2 \xrightarrow{AlBr_3} CH_3\overset{CH_3CH_2}{CH}{-}\overset{Br}{B}{-}C_2H_5} \qquad (3)$$

Unfortunately, the hydrogen bromide produced in the bromination stage (Equation 1) can create difficulties. Thus, it can protonolyse the product[1,4] or it can react with many groups which could be present in the original organoborane. Similarly, elemental bromine is a highly reactive reagent capable of attacking competitively with the desired substitution process. Consequently, it appeared desirable to develop alternative methods of introducing the α-bromosubstituent without using elemental bromine and without involving concurrent formation of hydrogen bromide.

N-Bromosuccinimide successfully achieved the α-bromination (Equation 4). However, the succinimide produced in the reaction served as a nucleophile to induce the rearrangement[2] of the desired α-bromoderivative. Consequently, this reagent was not suitable for the preparation of the desired α-bromotrialkylboranes.

The photochemically induced reaction of bromotrichloromethane has been utilized for the bromination of typical aliphatic hydrocarbons.[5] Consequently, we explored this possibility and, indeed, observed that radiation from a sun lamp induced the reaction of bromotrichloromethane with triethylborane to produce chloroform and the desired α-bromoethyldiethylborane.



(4)

In the usual reaction flask, equipped with a reflux condenser and maintained under nitrogen, was placed 14·2 ml (100 mmol) of triethylborane, 5 ml (50 mmol) of bromotrichloromethane, and 50 ml of methylene chloride.‡ The reaction was started by irradiation with a 275 w sun lamp, and followed by g.l.c. Bromotrichloromethane was completely consumed after 6 h. G.l.c. analysis showed the formation of chloroform (49·8 mmol) and a trace amount of ethyl bromide (< 0·5 mmol), and unused triethylborane (55 mmol).§ Distillation under reduced pressure gave 6·2 g (35 mmol) of α-bromoethyldiethylborane (70% yield based on $\mathrm{BrCCl_3}$); b.p. 57—58° (20 mm Hg). This compound was identified by its ^{1}H n.m.r. spectrum and its reactions.[2]

The reaction presumably proceeds through the same chain mechanism postulated for the corresponding reaction with aliphatic hydrocarbons (Equations 5, 6).[6]

$$\mathrm{Cl_3C{\cdot} + CH_3CH_2BEt_2 \longrightarrow CHCl_3 + CH_3\dot{C}HBEt_2} \qquad (5)$$

$$\mathrm{CH_3\dot{C}HBEt_2 + BrCCl_3 \longrightarrow CH_3CHBrBEt_2 + Cl_3C{\cdot}} \qquad (6)$$

Recently, the free-radical reactions of organoboranes have been the subject of intense investigation. It has been established that a major course of reaction is the attack of free radicals on boron with displacement of an alkyl group (Equation 7). Such free-radical displacements[7] have been

$$\mathrm{Y{\cdot} + BR_3 \longrightarrow YBR_2 + R{\cdot}} \qquad (7)$$

demonstrated for Y = RO,[8] $\mathrm{RO_2}$,[8,9] RS,[8,10] $\mathrm{R_2N}$,[8,11] and $\mathrm{RCH_2CH{=}CHO}$.[12] Indeed, only bromine atoms have previously been shown to achieve selective attack at the α-position of an alkyl group rather than attack at boron.[1,2]

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‡ An excess of triethylborane was used to minimize polybromination.

§ The recovery of more than 50 mmol of triethylborane indicates that a small amount of polybromination (*ca.* 5 mmol) occurred. In fact, the ^{1}H n.m.r. spectrum of the higher-boiling material in the product suggested the presence of the dibromide.

(It has been reported that in the gas phase the methyl free-radical can atttack at both positions.[13]) The present results reveal that the $Cl_3C\cdot$ free-radical resembles bromine atoms in this characteristic—it attacks the α-position preferentially with only minor attack on boron. The formation of 1% of ethyl bromide in the reaction of triethylborane presumably corresponds to the minor attack of the $Cl_3C\cdot$ radicals on boron with displacement of the ethyl group.

It is also possible to utilize the photochemical reaction of bromotrichloromethane followed by the addition of water to achieve a single migration.[14] Thus, the reaction of triethylborane under these conditions leads to s-butylethylborinic acid (76%). Similarly, tri-n-butylborane yields 4-octyl-n-butylborinic acid, converted by oxidation into octan-4-ol (60%). However, this feature was not investigated in detail since the chief advantage of the present process appears to be the direct synthesis of the α-bromo-derivatives without the problems involved in the use of reactive elemental bromine and the concurrent formation of hydrogen bromide.

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