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Preliminary communication

AN EXCEPTIONALLY FACILE HOMOLYTIC DISPLACEMENT IN THE REACTION OF NITROGEN TRICHLORIDE WITH TRIALKYLBORANES

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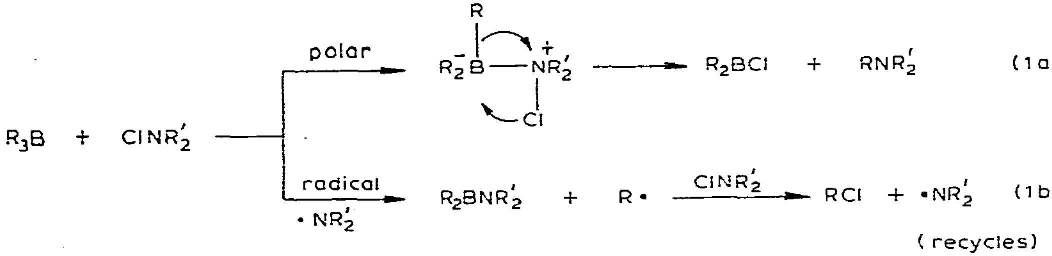
Summary

Nitrogen trichloride undergoes an exceptionally facile reaction with trialkylboranes, apparently by a free radical chain process involving a homolytic substitution at the boron center, providing a new route from organoboranes to the corresponding alkyl chlorides.

The reactions of *N*-chloroamines with trialkylboranes show a dichotomy of behavior which is of interest from both the synthetic and mechanistic viewpoints. Two competing pathways, one polar and one free radical, have been advocated to explain the concurrent formation of alkylamines (eq. 1a) and of alkyl chlorides (eq. 1b) in the reactions [1].



When R′ = H, the polar pathway (eq. 1a) is followed nearly exclusively, and provides a facile route to primary amines [2]. When R′ = CH_3, CH_2CH_3 or R'_2= $(CH_2)_5$, both pathways compete and approximately equal amounts of the alkyl chloride and tertiary amine are formed [1,3]. Interestingly, free radical scavengers can suppress the homolytic pathway so that the ionic pathway dominates. Thus, reaction of tri-*n*-butylborane with *N*-chlorodimethylamine in the presence of galvinoxyl produces only *n*-butyldimethylamine (eq. 1a) [1].

It occurred to us that the weakness of nitrogen trichloride as a base should also circumvent this dichotomy of mechanism and thereby favor the homolytic pathway. Treatment of tri-*s*-butylborane with one equivalent of nitrogen trichloride [4] in carbon tetrachloride at 0°C results in instantaneous decolorization of the yellow color. GLC analysis reveals the formation of one equivalent of *s*-butyl chloride, which does not increase with time (eq. 2). A second equivalent of nitrogen trichloride produces a second equivalent of *s*-butyl chloride in one hour (eq. 3). The reaction of a third equivalent of nitrogen trichloride is much slower, requiring 48 h for the formation of the third equivalent of *s*-butyl chloride (eq. 4). Overall the reaction converts tri-*s*-butylborane into *s*-butyl chloride in 94% yield.

Although we have not yet established the nature of the boron and nitrogen containing products, the stoichiometry would suggest the following sequence of reactions involving the formation of such derivatives (eq. 2—4).

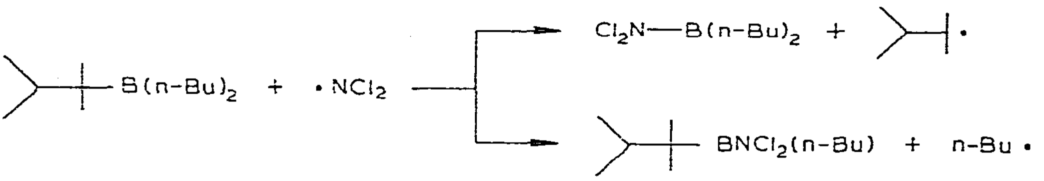
$$s\text{-}Bu_3B + NCl_3 \longrightarrow s\text{-}BuCl + s\text{-}Bu_2BNCl_2 \quad (2)$$

$$s\text{-}Bu_2BNCl_2 + NCl_3 \longrightarrow s\text{-}BuCl + s\text{-}BuB(NCl_2)_2 \quad (3)$$

$$s\text{-}BuB(NCl_2)_2 + NCl_3 \longrightarrow s\text{-}BuCl + B(NCl_2)_3 \quad (4)$$

The wide generality of the reaction is indicated by its ready applicability to tri-*n*-butyl-, triisobutyl-, tricyclopentyl- and tri-*exo*-norbornylborane.

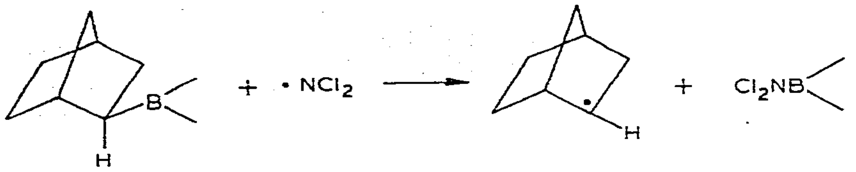
The reaction of trialkylboranes with nitrogen trichloride apparently follows the homolytic pathway (eq. 1b, R′ = Cl) to the exclusion of the polar process (eq. 1a). Evidence for a free radical pathway was obtained in competition experiments. Treatment of one equivalent of di-*n*-butylthexylborane with one equivalent of nitrogen trichloride provides 37% of *n*-butyl chloride and 44% of 2-chloro-2,3-dimethylbutane. Making the statistical correction for two *n*-butyl moieties, the results indicate that the tertiary thexyl group is greater than twice as reactive as the primary *n*-butyl groups. Evidently, this result is a consequence of the more favorable displacement of the tertiary (eq. 5a) versus a primary radical (eq. 5b) by the dichloroamino radical [5]. Electrophilic (polar) reactions of di-*n*-alkylthexylboranes react predominantly with the *n*-alkyl moieties [6].



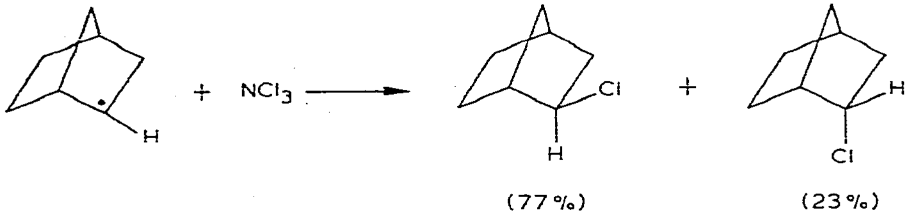
(5a)

(5b)

Additional evidence is provided by the reaction of nitrogen trichloride with pure tri-*exo*-norbornylborane which gives 77% *exo*- and 23% *endo*-2-chloronorbornane. This result is similar to the free radical autoxidation of tri-*exo*-norbornylborane which provides 86% *exo*- and 14% *endo*-norborneol [7]. The loss of stereospecificity is doubtless a result of the free radical nature of the reactions (eq. 6 and 7).



(6)



(7)

Alkaline hydrogen peroxide oxidation of tri-*exo*-norbornylborane gives 99.6% *exo*-norborneol [8].

The displacement of an alkyl radical from a trialkylborane by a dichloroamine radical (eq. 1b, R′ = Cl) is a remarkably facile process. The presence of 8 mole % of iodine, an exceptionally favorable inhibitor for the autoxidation of organoboranes [9], does not significantly inhibit the reaction of equimolar amounts of nitrogen trichloride and tri-*n*-butylborane. The iodine is decolorized virtually instantaneously and immediate GLC analysis indicates the formation of 83% *n*-butyl chloride and 15% *n*-butyl iodide*.

While the mechanistic aspects of the reaction of organoboranes with nitrogen trichloride are of special interest, the synthetic implications may be even greater. The reaction appears to provide a facile method for the conversion of trialkylboranes into alkyl chlorides in high yields, a procedure which is currently lacking. In addition, the reaction promises to provide a route to novel types of boron intermediates, such as R_2BNCl_2, $RB(NCl_2)_2$, and $B(NCl_2)_3$. We are currently exploring these possibilities.

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*Nitrogen trichloride does not decolorize iodine in the absence of organoborane.