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ORGANOBORANES FOR SYNTHESIS. 12. THE REACTION OF ORGANOBORANES WITH NITROGEN TRICHLORIDE. A CONVENIENT PROCEDURE FOR THE CONVERSION OF ALKENES INTO ALKYL CHLORIDES *VIA* HYDROBORATION[1]

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Abstract - Trialkylboranes are readily converted to the corresponding alkyl chlorides by a free radical reaction with nitrogen trichloride (NCl_3). Compared to many other chlorinating agents examined, NCl_3 is a superior reagent for the effective conversion of organoboranes into alkyl chlorides. Combined with the high regioselectivity inherent in the hydroboration reaction, the treatment with NCl_3 allows alkenes to be transformed into pure alkyl chlorides of predictable structure. This process constitutes a valuable method for the *anti*-Markovnikov hydrochlorination of alkenes in 66-94% yield. Experimental evidence indicates that this reaction proceeds via free radical intermediates. The reaction of organoboranes with NCl_3 is comparable to or better than other methods, such as those requiring refluxing aqueous cupric or ferric chloride, or those producing hydrogen chloride as a by-product. Consequently, this procedure could be very useful for the conversion of acid-sensitive (*e.g.*, certain bicyclic) alkenes into alkyl chlorides where extensive skeletal rearrangements occur in hydrogen chloride additions.

Since the discovery of hydroboration, it has become evident that simple procedures for the conversion of organoboranes into the corresponding alkyl halides would open new synthetic possibilities for these versatile boron intermediates. Such a procedure would constitute a method for the *anti*-Markovnikov hydrohalogenation of alkenes. We have reported that usually sluggish reactions of bromine[3] and iodine[4] with organoboranes are greatly accelerated by the presence of sodium methoxide and sodium hydroxide[5] providing excellent yields of the corresponding bromides and iodides (eq 1).

$$RCH{=}CH_2 + HB\langle \xrightarrow{THF} RCH_2CH_2B\langle \xrightarrow[NaOCH_3]{X_2} RCH_2CH_2X + NaX + CH_3OB\langle \qquad (1)$$

$X = Br, I$

Such base-induced halogenation reaction of organoboranes has been employed for the formation of relatively inaccessible bicyclic halides, such as endo-2-bromo- and -2-iodonorbornanes[6,7] and for the synthesis of chiral alkyl iodides of high optical purity[7]. Clearly, a convenient procedure for the conversion of organoboranes into the corresponding alkyl chlorides would be a valuable development.

Unfortunately, adaptation of these alkali-induced procedures for the reaction of chlorine with trialkylboranes is unsatisfactory. Mixtures of chlorine and aqueous sodium hydroxide form sodium hypochlorite which oxidizes trialkylboranes to alcohols[8]. Treatment of trialkylboranes with chlorine in the presence of sodium methoxide using the procedures employed for the facile bromination and iodination reactions gives complex mixtures and provides low yields (< 33%) of alkyl chlorides. In fact we found that reaction of tri-*n*-butylborane with chlorine gas in the absence of bases, as well as the reaction of a wide variety of common chlorinating reagents, such as sulfuryl chloride, phosphorous pentachloride, trichloromethanesulfonyl chloride, trichloromethanesulfenyl chloride, *N*-

N-chlorosuccinimide, or 1-chlorobenzotriazole, all gave poor results, providing only 1-25% yields of *n*-butylchloride[1b]. Previous reports in the literature for the reaction of chlorine with trimethylborane[9] and *n*-butylboroxine[10] indicate that substitution of the alkyl hydrogens occurs and no alkyl chlorides are produced.

Methods reported previously for conversion of trialkylboranes have given mixed results. Treatment of trialkylboranes with *t*-butyl hypochlorite utilizes only one of the alkyl groups, thus limiting conversion of an olefin into alkyl chloride *via* hydroboration to 33% (eq 2).[11]

$$R_3B + t\text{-}BuOCl \longrightarrow RCl + t\text{-}BuOBR_2 \qquad (2)$$

The conversion of trialkylboranes into alkyl chlorides by reaction with cupric or ferric chloride has given variable results in the hands of different workers (eq 3).[12-14]

$$R_3B + 4\,CuCl_2 \xrightarrow[65^\circ C]{THF/H_2O} 2\,RCl + RB(OH)_2 + 2\,Cu_2Cl_2 + 2\,HCl \qquad (3)$$

It is apparent that the reactions of trialkylboranes with cupric and ferric chloride can provide alkyl chlorides, but the reaction does have apparent disadvantages such as long reaction times (48 h) and the formation of hydrogen chloride, which could be deleterious if the trialkylborane possessed acid-sensitive functionalities. In addition, the refluxing aqueous reaction medium would presumably preclude the formation of easily hydrolyzed alkyl chlorides, such as norbornyl or other reactive bicyclic halides.

Trialkylboranes have been converted into the corresponding alkyl chlorides in 30-50% yields using *N*-chlorodialkylamines.[15] Unfortunately, this reaction is not suitable for the efficient preparation of alkyl chlorides, since the concurrent polar and radical processes occur to give amines and alkyl chlorides respectively (eq 4).[16]

$$R_3B + ClNR'_2 \begin{cases} \xrightarrow{\text{polar}} R_2\overset{R}{B}\!-\!\overset{+}{N}R'_2\,(Cl) \longrightarrow R_2BCl + RNR'_2 \\ \xrightarrow{\text{radical}} R_2BNR'_2 + R\cdot \xrightarrow{ClNR'_2} RCl + \cdot NR'_2 \text{ (chain)} \end{cases} \qquad (4)$$

When R' = H, the polar pathway becomes the preferred course and provides a useful route to amines.[17] When R' = alkyl, such as methyl or *n*-butyl, both pathways compete effectively.[16] The synthesis of alkyl chlorides *via* reaction of trialkylboranes with dichloramine-T has been reported in the literature (eq 5)[18].

$$R_3B + Cl_2NSO_2C_6H_4CH_3 \longrightarrow RCl + R_2BNClSO_2C_6H_4CH_3 \qquad (5)$$

It occurred to us that an *N*-chloramine possessing a weak nitrogen-chlorine bond and having low basicity toward boron would favor the homolytic process over the polar pathway. Nitrogen trichloride appeared to be a reagent possessing these desirable characteristics. Accordingly, we examined nitrogen trichloride as a possible new chlorinating reagent for the conversion of trialkylboranes into alkyl chlorides.

RESULTS AND DISCUSSION

Nitrogen trichloride (NCl_3), readily prepared from calcium hypochlorite, ammonium chloride and HCl, is stable and safe to handle, with simple precautions.[19] Treatment of tri-*s*-butylborane at 0°C in methylene chloride or carbon tetrachloride with one equiv of NCl_3 in the corresponding solvent under the normal laboratory light results in an instantaneous decolorization of the yellow NCl_3, producing one equiv of *s*-butyl chloride (eq 6).

$$(s\text{-}Bu)_3B + NCl_3 \longrightarrow s\text{-}BuCl + (s\text{-}Bu)_2BNCl_2 \qquad (6)$$

Addition of a second equiv of NCl_3 results in a slower reaction, consuming the reagent in 1 h and forming a second equiv of *s*-butyl chloride (eq 7).

$$(s\text{-Bu})_2BNCl_2 + NCl_3 \longrightarrow s\text{-BuCl} + s\text{-BuB}(NCl_2)_2 \quad (7)$$

A final equiv of NCl_3 converts the third alkyl group to alkyl chloride much more slowly, requiring 48-72 h for completion. Overall, treatment of tri-*s*-butylborane with three equiv of nitrogen trichloride produces a 94% yield of *s*-butyl chloride (eq 8).

$$(s\text{-Bu})_3B + NCl_3 \longrightarrow 3\,s\text{-BuCl} + B(NCl_2)_3 \quad (8)$$

Reaction of Representative Trialkylboranes. Representative organoboranes (10 mmol) derived from terminal, internal, cyclic and bicyclic alkenes were treated with NCl_3 (30 mmol). The reaction was allowed to proceed until the yellow color of NCl_3 disappeared. The trialkylboranes derived from internal alkenes react relatively faster. Tri-*i*-butylborane, containing β-methyl alkyl groups, reacts unusually slowly. This is similar to the autoxidation of organoboranes with oxygen.[20,21]

As described above, in the reaction of trialkylboranes with NCl_3, the first equiv of alkyl chloride is formed almost instantaneously and the second equiv is formed in 1 h. Apparently, the third step is so slow that other side-reactions, such as the decomposition of NCl_3 or the proton abstraction from the alkyl chain, may occur. However, the results summarized in Table I reveal that the conversion of alkenes into alkyl chlorides *via* hydroboration, followed by the reaction with NCl_3, provides an excellent procedure for the synthesis of a wide variety of alkyl chlorides.

Table 1. Conversion of alkenes into alkyl chlorides via hydroboration and reaction with nitrogen trichloride[a]

Alkene	Time[b] h	Product[c]	Yield[d] %
1-butene	72	1-chlorobutane	74
2-methyl-1-propene	240	1-chloro-2-methyl propane	86
2-butene	48	2-chlorobutane	94
cyclopentene	30	chlorocyclopentane	69
cyclohexene	48	chlorocyclohexane	69
norbornene	72	2-chloronorbornane	66(56%)[e]

[a]Reaction of R_3B (10 mmol) with NCl_3 (30 mmol); addition of NCl_3 at 0°C, followed by stirring at 25°C for the time indicated. [b]Time for disappearance of the yellow color of NCl_3. [c]All products characterized by comparison with authentic samples. [d]Yields based on starting alkenes determined by GC (conditions: 10% DC 710 on Chromosorb W; 6 ft x 0.25 in); value in parenthesis is isolated yield. [e]Stereochemistry by ^1H NMR is 77% *exo*- and 23% *endo*-.

Reaction of Mixed Organoboranes. In the formation of alkyl chlorides from trialkylboranes, the transformation of the third alkyl group is slow and incomplete, as indicated by low yields (~ 66%) of alkyl chlorides formed (Table 1). The failure to use all three alkyl groups could limit the synthetic utility of the reaction if a valuable alkene is used for hydroboration. In order to circumvent this difficulty, the reaction of mixed organoboranes containing alkyl- or heteroatom-substituted blocking groups was examined.

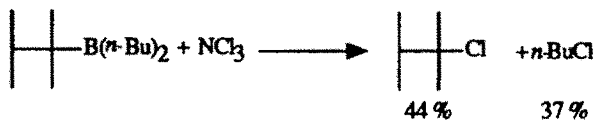
A study of the reaction of NCl_3 with *n*-butylborane derivatives revealed partially encouraging results (Table 2). Methyl di-*n*-butylborinate reacts very sluggishly. *n*-Butyldichloroborane also reacts relatively slowly, while di-*n*-butylchloroborane reacts in less than 1 min. However, the low yields of *n*-butyl chloride in all of these cases suggest that some other pathway is being followed. In the case of thexyldi-*n*-butylborane, the thexyl group participates in the reaction to a larger extent (eq 9). The *B*-cyclooctyl bond of *B*-*n*-butyl-9-borabicyclo[3.3.1]nonane apparently competes with *B*-*n*-butyl group, providing only 48% of *n*-butyl chloride. However, the use of two equiv

of NCl_3 increases the yield of *n*-butyl chloride to 81%

Table 2. Reaction of one equivalent of nitrogen trichloride with *n*-butylborane derivatives[a]

Organoborane	Reaction Time[b] min	Yield[c] %
di-*n*-butylthexylborane	60	37[d]
B-*n*-butyl-9-BBN	< 1	48[e]
n-butyldichloroborane	120	~ 5
di-*n*-butylchloroborane	< 1	17
methyl di-*n*-butyl borinate	1080	3

[a] Borane substrate (10 mmol) and NCl_3 (10 mmol). [b] Time for disappearance of NCl_3 color. [c] Yield determined by GC and based on NCl_3. [d] Thexyl chloride was detected in 44% yield. [e] Twenty mmols of NCl_3 are decolorized in 60 min and the yield of 1-chlorobutane is 81% based on organoborane.



(9)

Mechanism. The reaction of trialkylboranes with *N*-chlorodialkylamines is complicated by competing polar and radical processes (eq 4).[16] On the other hand, chloramine reacts with trialkylboranes solely by polar process, providing primary amines (eq 10).[17]

$$R_3B + ClNH_2 \xrightarrow{\text{aq NaOH}} R_2BOH + NaCl + RNH_2 \quad (10)$$

In the polar pathway, *N*-chloramine substrate apparently coordinates with boron, followed by an alkyl group migration to the adjacent nitrogen atom with the displacement of halogen (eq 11).

$$R_3B + ClNR'_2 \rightleftharpoons R_2\overset{R}{\underset{-}{B}}-\overset{+}{\underset{Cl}{N}}R'_2 \longrightarrow R_2B-\overset{R}{\underset{+}{N}}R'_2Cl^- \xrightarrow{\text{NaOH}} R_2BOH + RNR'_2 + NaCl \quad (11)$$

In the radical pathway, an aminyl radical attacks at the boron with displacement of an alkyl radical. The alkyl radical abstracts chlorine from the *N*-chloramine substrate to give alkyl chloride and aminyl radical which continues the chain (eqs 12, 13).

$$R_3B + \cdot NR_2 \longrightarrow R_2BNR'_2 + R\cdot \quad (12)$$

$$R\cdot + ClNR'_2 \longrightarrow RCl + \cdot NR'_2 \longrightarrow \text{chain} \quad (13)$$

When R' = H, the polar pathway is followed principally or completely, leading to amine products. When R' = methyl or *n*-butyl, both pathways compete about equally. With *N*-chlorodialkylamines, addition of a radical inhibitor, such as galvinoxyl, suppresses the radical pathway, and the organoborane reacts completely by the polar pathway, giving tertiary amines. However, the polar pathway cannot be suppressed and the reaction is not efficient as a route to alkyl chlorides.

It is difficult to separate the factors governing the pathway which should be followed. It seemed reasonable that an *N*-chloramine, possessing a weak chlorine-nitrogen bond and having low basicity toward boron, would favor the homolytic process over the polar pathway, which seemingly requires prior coordination of the *N*-chloramine to boron. It appeared that an *N*-chloramine reagent possessing these characteristics is nitrogen trichloride. The dissociation energy of the nitrogen-chlorine bond is only 47.7 kcal/mol[22] (cf. Cl-Cl = 58.0 kcal/mol), a feature which could permit easy homolysis of the nitrogen-chlorine bond under radical conditions. Due to three electron-withdrawing chlorine substituents, NCl_3 should also be a weaker base than chloramine or *N*-chlorodialkylamines.

Experimental evidence indicates that the reaction of trialkylboranes with NCl_3 is a free radical process. For example, tri-*n*-butylborane reacts with two moles of NCl_3 in 1 h. The reaction of the third mole of NCl_3 proceeds slowly, producing 2.22 mmol of *n*-butyl chloride along with 0.21 mol of *s*-butyl chloride. Since the hydroboration of 1-butene produces 6-7% of organoboranes with boron at the secondary position, all available *s*-butyl groups are employed in the reaction.

This behavior is typical of free radical reactions involving organoboranes containing mixed primary and secondary alkyl groups.[20] Evidently, radical displacement of *s*-alkyl groups gives more stable radicals than the displacement of *n*-alkyl groups. This may be contrasted with heterolytic reactions of organoboranes, such as protonolysis, where primary groups react faster than secondary groups.[23]

In the case of tri-*s*-butylborane, all three alkyl groups are utilized on treatment with three equivalents of NCl_3. The first two alkyl groups are converted to *s*-butyl chloride in about 1 h, the third requiring 72 h for the complete conversion.

Another experiment that suggests the involvement of free radicals is the reaction of thexyldi-*n*-butylborane with NCl_3 (eq 9). The product distribution indicates a high preference for the formation of thexyl chloride.

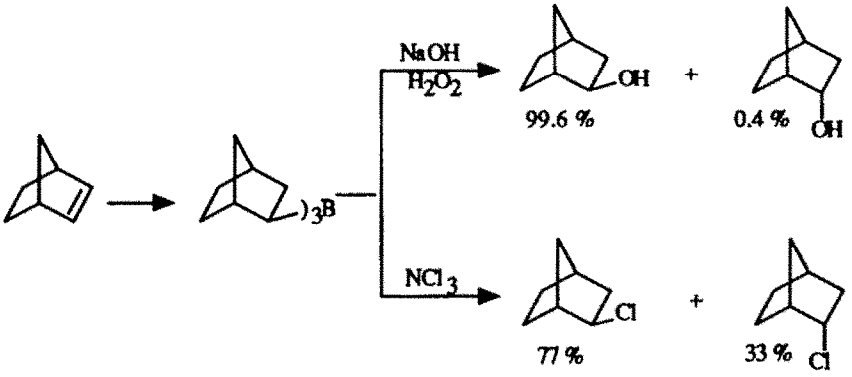
Thexyldialkylborane reactions involving non-radical processes are characterized by the extremely low aptitude of the thexyl group to participate in the reactions.[24] It is evident in the nitrogen trichloride reaction that the large amount of thexyl chloride formed is suggestive of a homolytic process, a more stable thexyl radical being displaced in preference to a primary butyl radical.

The reaction of tri-*n*-butylborane with 3 equiv of NCl_3 is greatly accelerated in the presence of a sunlamp, consuming 3 mmol of NCl_3 in 1 h, rather than the 72 h needed in the presence of normal laboratory light. Unfortunately, the yield of *n*-butyl chloride drops to 1.45 equiv and is accompanied by the formation of a mixture of dichlorobutanes and 0.91 equiv of chloroform. Under these conditions, tri-*s*-butylborane gives 1.50 equiv of *s*-butyl chloride, 0.51 equiv of chloroform and 0.36 equiv of dichlorobutanes. The chloroform is evidently formed from chlorination of the solvent, methylene chloride, and the dichlorobutanes from chlorination of the initially formed butyl chlorides. By carrying out the reaciton in carbon tetrachloride, chlorination of the solvent is avoided. However, no increase in the yields of *n*-butyl or *s*-butyl chloride is observed. Instead, the amount of dichlorobutanes is increased. Further proof for the involvement of radical intermediates is provided by inhibition studies.

Inhibition of Chlorination Reaction. Iodine is an exceptionally powerful inhibitor for the free radical oxidation of trialkylboranes with molecular oxygen.[25] However, treatment of tri-*n*-butylborane with 1 mol of nitrogen trichloride in the presence of 8 mol percent of iodine results in the immediate disappearance of the iodine color. (Iodine and NCl_3 do not react in control experiments.) There is formed 0.83 equiv of *n*-butyl chloride, 0.04 equiv of *s*-butyl chloride, 0.16 equiv of *n*-butyl iodide and a trace of *s*-butyl iodide. Since iodine and tri-*n*-butylborane do not react under these conditions,[5] it appears that the alkyl iodide is formed by the reaction of molecular iodine with displaced alkyl radicals. However, the free radical reaction of trialkylboranes with nitrogen trichloride must be an exceptionally favorable process not to be noticeably inhibited by iodine.

Stereochemistry of Chlorination. It is interesting to note that the organoborane from norbornene is converted by alkaline hydrogen peroxide into 99.6% *exo*-norborneol.[23] However, there is a considerable loss of stereochemistry in the reaction with NCl_3 (eq 14). Such loss of stereospecificity is presumably a result of the free radical nature of the reaction. The free radical oxidation of tri-*exo*-norbornylborane with molecular oxygen provides 86% *exo*- and

14% *endo*-norborneol.[26]



(14)

Irrespective of the precise mechanism of the reaction of nitrogen trichloride with organoboranes, the procedure offers promise as a convenient method for the *anti*-Markovnikov hydrochlorination of alkenes *via* hydroboration. A general study of the reaction with representative organoboranes reveals that in general only two of the three alkyl groups of the trialkylborane are utilized in reasonable reaction times.

CONCLUSIONS

It is evident that the reaction of trialkylboranes with nitrogen trichloride provides a convenient procedure for the synthesis of alkyl chlorides under non-acid conditions in yields exceeding those of other methods. It also appears that novel compounds, such as R_2BNCl_2, $RB(NCl_2)_2$ and $B(NCl_2)_3$ are formed in the reaction and may have exciting chemistry awaiting their exploration.

With the discovery of the NCl_3 reaction, the synthetic chemist now has a simple procedure for conversion of alkenes into alkyl chlorides in good yields *via* hydroboration, thus complementing the existing bromination and iodination procedures for converting trialkylboranes into the corresponding alkyl bromides and alkyl iodides. A disadvantage of this procedure is that only two groups of the trialkylboranes are readily accommodated in the reaction. Hopefully, this drawback can be circumvented by the application of mixed alkylborane derivatives.

EXPERIMENTAL SECTION

General Comments. The experimental techniques employed for handling air-sensitive materials and for the purification of solvents are described elsewhere.[23] All glassware was oven-dried at 140°C for at least 4 h before use, assembled hot, and cooled under a stream of purified nitrogen. Materials were transferred using oven-dried, nitrogen flushed syringes fitted with stainless steel needles. Larger volumes of liquids were transferred using double-ended needles. All reactions were run under a nitrogen atmosphere. CAUTION: Pure nitrogen trichloride is treacherously explosive at its boiling point (~71°C) in the presence of light or in contact with certain organic materials.[29]

Materials. Alkenes were obtained from various commercial sources and purified, if necessary, by distillation under nitrogen from lithium aluminum hydride. All solvents (Mallinckrodt Spectranalysed or Analytical Reagent) used in the chlorination studies were deoxygenated by bubbling nitrogen through a gas-dispersing tube, and stored under a nitrogen atmosphere over molecular sieves. Approximately 1-*M* solutions of nitrogen trichloride in methylene chloride or carbon tetrachloride were prepared and standardized according to a literature procedure.[18] The bright yellow solutions of NCl_3 showed negligible decomposition (1.5% in 2 months) when stored in complete darkness at -5°C. Tri-*n*-butyl- and tri-*i*-butylborane (Callery) were distilled under nitrogen before use. Tri-*s*-butylborane, di-*n*-butylchloroborane, di-*n*-butylmethoxyborane and *n*-butyldichloroborane were prepared and purified exactly, or in direct analogy, as the previously described methods.[23] Borane-methyl sulfide (Aldrich) was used as received. Borane-tetrahydrofuran and 9-BBN were prepared and standardized as previously described.[23]

Analyses. GC analyses were carried out using the necessary packed column to effect separation of the components. ^1H NMR spectra were recorded in $CDCl_3$ on a Varian T-60 (60MHz) spectrometer using tetramethylsilane as an internal standard (δ 0 ppm). The alkyl chlorides formed in this study were identified by (GC and/or ^1H NMR) comparison with authentic samples which were either commercially available or synthesized by literature procedures.

Reaction of Nitrogen Trichloride with Tri-*n*-butyl- and Tri-*s*-butylborane: Stoichiometry Investigations. In the first experiment utilizing NCl_3, a 50-mL flask equipped with magnetic stirrer, septum inlet, and pressure-equalizing addition funnel was flushed with nitrogen. The flask was charged with 10 mmol (2.42 mL) of tri-*n*-butylborane and 10 mL of methylene chloride and cooled to O°C. 10 mmol (7.81 mL of 1.28 *M* solution) of NCl_3 in methylene chloride was placed in the addition funnel and added dropwise to the reaction mixture over 10 min. The bright yellow color of NCl_3 disappeared instantaneously as it was added, leaving a colorless solution. Then *n*-heptane was added as internal standard. GC analysis indicated the clean formation of 10.5 mmol of *n*-butyl chloride and 0.7 mol of *s*-butyl chloride. The yields did not change in 1 h. The by-product was expected to be $(n\text{-}C_4H_9)_2BNCl_2$, a species which could undergo rearrangement to $Cl_2BN(n\text{-}C_4H_9)_2$. Treatment of 2-mL aliquot of the reaction mixture with 1 mL of 6 *N* aqueous NaOH under nitrogen resulted in an exothermic reaction, but no di-*n*-butylamine or any other products higher boiling than *n*-heptane were detected by GC analysis. Similar treatment of an aliquot with 6 *N* HCl resulted in an exothermic reaction. The organic layer contained only butyl chlorides and *n*-heptane. The aqueous layer was neutralized with 6 *N* NaOH and extracted with methylene chloride. Again, no additional products were observed by GC analysis. In another experiment, 2 mmol of tri-*n*-butylborane was treated with 6 mmol of NCl_3 using the procedure described above. After 1 h, internal standard was added to the yellow solution. Analysis by GC indicated the formation of 3.91 mmol (65%) of *n*-butyl chloride. The yield increased to 4.38 mmol in 2.5 h and 4.45 mmol (74%) in 3.5 h, but showed no further increase after 24 or 53 h and the yellow color of NCl_3 persisted along with small amounts of precipitate. Nearly identical results were obtained in carbon tetrachloride solvent. The reaction required 1 equiv of NCl_3 per butyl group of the tri-*n*-butylborane. When 2 mmol of tri-*n*-butylborane was treated with 1 mmol of NCl_3 in methylene chloride, immediate GC analysis indicated the formation of 0.96 mol of *n*-butyl chloride and 0.05 mol of *s*-butyl chloride. All of the volatile components were removed *via* aspirator and the residual material oxidized with alkaline hydrogen peroxide. GC analysis indicated the presence of 3.80 mmol *n*-butyl alcohol and 0.17 mol *s*-butyl alcohol. Thus, the total yield of *s*-butyl groups as alcohol and chloride was 0.22 mol. The total yield of *n*-butyl groups found as alcohol and chloride was 4.76 mmol. The results indicated that 1 mmol of *n*-butyl group was unaccounted for since independent alkaline hydrogen peroxide oxidation of 2 mmol of the starting organoborane produced 5.75 mmol of *n*-butyl alcohol and 0.22 mol of *s*-butyl alcohol. The reaction of tri-*s*-butylborane with 3 equiv of NCl_3 was examined in the same way as the reaction with tri-*n*-butylborane. The yield of *s*-butyl chloride was 63% in 1 h, 67% in 3 h, and 84% in 28 h. After 72 h, the reaction mixture was colorless, but contained a white precipitate. A quantitative yield of *s*-butyl chloride was observed. In carbon tetrachloride solvent, the yield was 94% in 48 h and some yellow color persisted.

Reaction of NCl_3 with Tri-*n*-butylborane in the Presence of Iodine. In the reaction apparatus described above was placed 0.16 mmol (8 mol %) of iodine, 2 mmol of tri-*n*-butylborane and 2 mL of methylene chloride. Addition of 2 mmol of NCl_3 in methylene chloride resulted in immediate decolorization of the purple solution. Addition of *n*-heptane as internal standard and GC analysis indicated the formation of 1.66 mol of *n*-butyl chloride, 0.07 mol *s*-butyl chloride, 0.31 mol *n*-butyl iodide and a trace of *s*-butyl iodide.

Reaction of NCl_3 with Tri-*n*-butyl- and Tri-*s*-butylborane in the Presence of a Sunlamp. The usual reaction apparatus was charged with 2 mmol of tri-*n*-butylborane and 2 mL of methylene chloride and cooled to O°C. Then 6 mmol of NCl_3 in methylene chloride was added and the reaction mixture irradiated with a Sears 275 W sunlamp. After 1 h, the reaction mixture was completely decolorized and contained a white precipitate. After addition of *n*-heptane as an internal standard, GC analysis indicated the formation of 2.90 mmol of *n*-butyl chloride, 1.43 mol chloroform and a mixture of dichlorobutanes. When the reaction was repeated in carbon tetrachloride (using NCl_3 in carbon tetrachloride), the formation of chloroform from chlorination of methylene chloride was avoided. However, the yield of *n*-butyl chloride decreased to 2.33 mmol and the amount of dichlorobutanes increased. The photochemical reaction of 2 mmol of tri-*s*-butylborane and 6 mmol NCl_3 in methylene chloride produced 3.00 mmol *s*-butyl chloride, 1.02 mmol chloroform, and 0.71 mmol of dichlorobutanes. The distribution of the 3 to 4 dichlorobutane isomers observed in these experiments was not determined. They were identified as dichlorobutanes by co-injection of an authentic mixture.

Conversion of Norbornene into 2-Chloronorbornane: General Procedure. Approximately 1 *M* of nitrogen trichloride solution in carbon tetrachloride was prepared according to a published procedure.[19] A dry, 500-mL flask equipped with septum inlet, magnetic stirrer, and pressure-equalized addition funnel was charged with norbornene (14.3 g, 150 mmol), flushed with nitrogen and maintained under a static pressure of the gas until workup. Tetrahydrofuran (80 mL) was added and the reaction mixture cooled to O°C in an ice bath. Conversion to the trialkylborane was achieved by the dropwise addition of borane-tetrahydrofuran (20.8 mL of a 2.44 *M* solution, 50 mmol) through the septum inlet. After stirring 1 h at room temperature, the tetrahydrofuran was completely removed by aspirator vacuum and replaced by carbon tetrachloride (50 mL). The reaction mixture was cooled to O°C and nitrogen trichloride (169 mL of a 0.89 *M* solution in carbon tetrachloride) was placed in the addition funnel and added dropwise to the reaction mixture over 15 min. The ice bath was removed and the reaction allowed to stir in normal laboratory light until the reaction mixture became colorless and a white precipitate formed (48-72 h). The reaction mixture was treated with saturated aqueous sodium thiosulfate (100 mL) and the organic layer was removed, filtered, and dried over anhydrous potassium carbonate. Distillation under vacuum gave 2-chloronorbornane. Yield: 11.0 g (56%); bp 73°/35 mm; $n^{20}D$ 1.4853 [lit.[30] for *exo*-2-chloronorbornane: bp 75°/41 mm; $n^{20}D$ 1.4849]. ^1H NMR ($CDCl_3$): δ 0.8-2.4 (m,10H), 3.85 (m,C-2 *exo*-methine), 4.0-4.4 (m, C-2 *endo*-methine). Integration of the

resonances of δ 3.85 and 4.0-4.4 indicated the isomer mixture consisted of 77% *exo*- and 23% *endo*-2-chloronorbornane.[31]

Reaction of NCl_3 with Mixed Borane Derivatives. Thexyldi-*n*-butylborane (4 mmol) in 4 mL of methylene chloride at 0°C was reacted with 4 mmol of NCl_3 in methylene chloride using procedures described above. Decolorization of NCl_3 required 60 min, after which time, internal standard was added. GC analysis indicated the formation of 1.48 mmol of *n*-butyl chloride, 0.03 mmol *s*-butyl chloride, 1.75 mmol of thexyl chloride, and 0.03 mmol of dichlorobutanes. Reaction of 4 mmol di-*n*-butylchloroborane under similar conditions resulted in immediate decolorization of the NCl_3 (4 mmol). GC analysis of the reaction mixture indicated a complicated reaction mixture containing 0.68 mmol of *n*-butyl chloride. Treatment of 2 mmol of di-*n*-butylmethoxyborane with 2 mmol of NCl_3 resulted in a very slow reaction. After 18 h, a precipitate formed and the reaction mixture was orange colored. GC analysis of the complex reaction mixture indicated that 0.07 mmol of *n*-butyl chloride was present. Reaction of *n*-butyldichloroborane with 1 equiv of NCl_3 required 2 h to decolorize and left a white precipitate. The reation mixture was very complex and only contained small amounts of *n*-butyl chloride. Treatment of 4 mmol B-*n*-butyl-9-borabicyclo[3.3.1]nonane with 4 mmol NCl_3 in methylene chloride resulted in instantaneous decolorization of the NCl_3. GC analysis indicated the formation of 1.92 mmol of *n*-butyl chloride. About 10% of the organoborane was unreacted. Four additional mmol of NCl_3 was added when decolorization required 60 min. GC analysis indicated the total yield of *n*-butyl chloride to be 3.23 mmol. Small amounts of dichlorobutanes and unidentified material were also observed.

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REFERENCES AND NOTES

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