

Exchange Reactions
of Organic Halides and Organo-silicon Compounds
with Boron Tribromide and Boron Triiodide

by

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To Carol.

ABSTRACT

Reactions of the boron halides with organic halides and organo-silicon compounds have been investigated. The results show exchange of halogens between the BX_3 ($X = Br, I$) and the organic halide, exchange of the halogen of the C-X bond being proved. The rates of halogen exchange vary. Reaction of the heavier halides with organo-silicon compounds indicated that the silicon-carbon bonds ruptured in the absence of electronegative atom attached to the silicon. The presence of an electronegative atom (halogen or oxygen) attached to the silicon causes the bond between the silicon and the electronegative atom to be preferentially broken. Products of exchange reactions of the boron halides and the organic halides or the organo-silicon compounds were studied by use of 1H NMR and GC/MS. From these results some possible mechanisms for the exchange reactions are postulated, but further work is indicated to prove the real courses of the reactions.

ACKNOWLEDGEMENTS

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INTRODUCTION

INTRODUCTION

Part I

There has been a growing recognition of the prevalence of redistribution reactions in both organic and inorganic chemistry. Where once they were discovered by chance, they are now systematically investigated, particularly in main group chemistry. Their peculiar fascination seems to lie in kinetic and thermodynamic characteristics, particularly of the random scrambling variety of reaction. Considerable information has been published concerning the kinetics and thermodynamics of redistribution reactions and studies have extended to at least sixty of the elements of the Periodic Table.

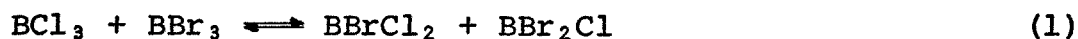
The acceptor characteristics of Group III compounds are probably the most important factors in producing the redistribution reactions, so well documented for this group, these usually being rapid and random. For unassociated three-coordinate monomers such as boron, aluminum, gallium, indium, and thallium compounds, four-center mechanisms are often proposed modeled on the structure of diborane or Al_2Cl_6 but for dimers the four-center transition state is often ruled out by virtue of being the starting structure. One of the factors which is responsible for somewhat different rate and thermodynamic characteristics than

customary in redistribution is the dimerization of many boron and aluminum compounds.

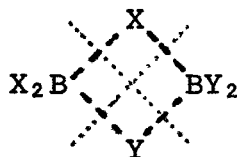
A considerable number of exchange processes at boron have been investigated. The most extensive work is with organoboron compounds, where some fortunate circumstances have enabled features of several mechanisms to be established with detailed kinetic work^{70,88}. First, the "bridged dimer" often postulated as the transition state for a closed four-centre mechanism is a stable species in boron chemistry. This is because of the existence of diborane and other bridged borane species. However, diborane itself undergoes slow scrambling of bridged and terminal hydrogen, which has been monitored by using isotopes of either boron or hydrogen^{56,57,97,128}. Secondly, the organic residue in alkylboron compounds gives a proton resonance which exhibits chemical shifts in different environments of sufficient magnitude for kinetic work. Thirdly, the dramatic coalescence of NMR signals with temperature can be observed, because the activation energies are sufficiently great^{4,66,85,108}. Some equilibrium constants are also available^{114,115}.

Boron halides are among the most reactive reagents in both organic and inorganic chemistry. The boron halides are likely to be reactive both for kinetic (they are among the strongest of electrophiles) and also for thermodynamic reasons. The latter features become particularly significant in thermochemical bond strengths.

Simple boron halides undergo mutual scrambling reactions on mixing. It has been found⁹² that boron trichloride and boron tribromide equilibrated over a period of several hours at 20° according to Eq. 1. Isolation of the components of the equilibrium mixture proved to be impossible at temperatures

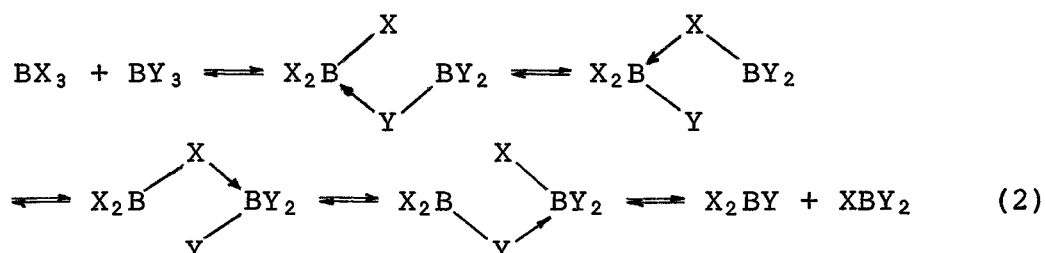


as low as -50° probably due to a rapid exchange reaction proceeding by means of a bridged structure such as:



All components of the equilibrium mixture can be formed once such a bridge has been formed. It can dissociate by the two different cleavages as indicated above. However, it has been found that the halogen exchange reaction for the boron trifluoride-boron trichloride system using infrared spectroscopy¹⁰⁵ has an unusually high activation energy, which would seem to be inconsistent with the described bridge mechanism. Since an initial breaking of bonds is not required, such an exchange mechanism should have a low activation energy. The high activation energy could also suggest that the rate determining step involves the weakening of the BF π bonds and a change in geometry from planar to tetrahedral. The high activation energy for the BF₃/BCl₃ system may be due to the

higher bond energy of the B-F bond as compared to the other boron-halogen bonds. Relatively lower boron halogen bond energies in the case of BCl_3 and BI_3 could be the major factor contributing to the four-centre transition state, thereby leading to a low activation energy for the exchange reaction. An alternative "four-centre" sequential rather than concerted mechanism would involve the intermediates shown in Eqn. 2.



Any mode of bond-breaking might be involved. From the kinetic studies, it has been found that in most of the systems studied, the reactions follow second-order kinetics, indicating that both the molecules are involved in the rate-determining step of the reaction. The real nature of the bond breaking in the four-centre intermediate is still unsolved. A relevant discussion on this point for another series of reactions tries to distinguish between the "open" (one of the four bonds absent) and "closed" (all four bonds present at the same time) structure for a transition state or reaction intermediate by describing more precisely the potential energy surfaces¹.

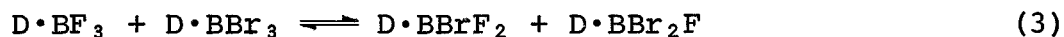
In general, the mixed halides BX_2Y and BXY_2 have all been identified either by $^{11}\text{B}^{58}$ or by ^{19}F NMR^{19,35} and/or

by their mass spectra^{19,84} and infrared or Raman spectra^{34,67,72,89,92}. Scrambling of halogen on boron in a reaction with a short half-life (measured in seconds, except for F-Cl exchange, (Eq. 2, X = Cl, Y = F)) is sufficiently slow for separate ¹¹B NMR signals to be observed for each mixed species present. It appears to be contradictory to the earlier work¹⁰⁵. In this rate region it has proved difficult to obtain other than qualitative rate data. The equilibrium always shows approximately random halogen distribution⁸⁵, but is too rapidly attained in either direction for the mixed halides to be isolated as a pure species⁹¹. Thus in systems such as the free boron trihalides^{90,91,95} and diboron tetrahalides¹¹⁹, halogen exchange is rapid enough to prevent the isolation of the mixed-halogen species but is slow on the NMR time scale so that separate resonances can be observed for the mixed and unmixed species.

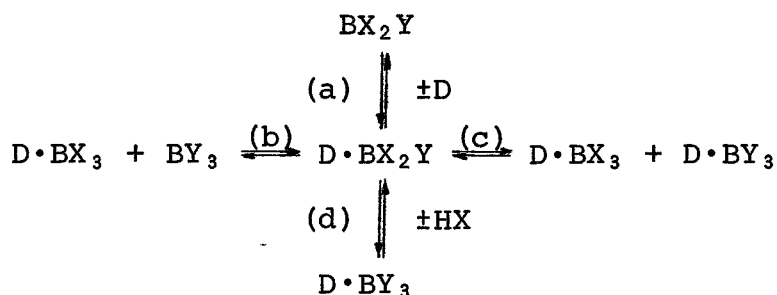
Earlier reports suggested that the halogen exchange reaction between boron tribromide and boron triiodide is considerably less facile than with the lighter sets of trihalides since Besson has claimed that he isolated both BBr₂I and BBrI₂. These mixed halides have been prepared by the reaction between boron tribromide and hydrogen iodide at 300 to 400°¹⁵ but modern work shows this to be in error.

Slower halogen scrambling is normally observed when the boron is made 4-coordinate (Eq. 3 and Scheme I) and consequently mixed halide complexes are isolated^{12,13}. For a

number of 4-coordinate boron systems (Eq. 3) with halogen substituents, the rate behaviour was found to be strongly dependent on the individual substituents on the boron.



The reaction was found to be slower when D is another halogen⁶⁹ than with trigonal boron halides, in contrast with an earlier report⁸⁰. When D forms a neutral adduct, its dissociation energy is apparently critical^{12,13,23}; scrambling is rapid for relatively weak adducts like those of dimethyl ether but very slow for strong adducts like the trimethyl amine.



Scheme I

Scheme I shows (by stoichiometry only) a number of paths by which mixed halide adducts have been made²³. That step (c) is difficult for strong adducts is indicative of an adduct dissociation requirement. Mixed halides of strong adducts cannot be made by step (c) even on heating to 180°^{12,13}.

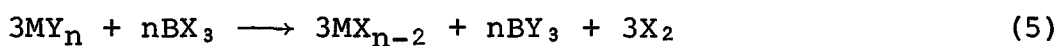
TABLE I

Products of Reactions of MX_n with BY_3

Boron halide	MX_n	Product	Reference
BBr_3	SbF_3	SbBr_3	53
BBr_3	UF_6	UBr_6	40
BBr_3	ReF_6	ReBr_5	27
BBr_3	GeH_3Cl	GeH_3Br	36
BI_3	AgF	AgI	98
BCl_3	XeF_4	XeCl_4	10
BCl_3	SF_4	SCl_4	33
BX_3 (X = I, Br)	$(\pi\text{-C}_5\text{H}_5)_2\text{MCl}_2$ (M = Ti, Zr, Hf)	$(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2$ (X = Br, I)	41
BBr_3	AlCl_3	AlBr_3	42
BBr_3	TlCl	TlBr	42
BBr_3	SnCl_4	SnBr_4	42
BBr_3	PhPCl_2	PhPBr_2	42
BBr_3	AsCl_3	AsBr_3	42
BBr_3	SbCl_3	SbBr_3	42
BBr_3	SbCl_5	SbBr_3	42
BBr_3	BiCl_3	BiBr_3	42
BBr_3	SOCl_2	SOBr_2	42
BBr_3	TiCl_3	TiBr_3	42
BBr_3	TiCl_4	TiBr_4	42
BBr_3	ZrCl_4	ZrBr_4	42
BBr_3	HfCl_4	HfBr_4	42
BBr_3	VCl_3	VBr_3	42
BBr_3	VOCl_3	VOBr_2	42
BBr_3	NbCl_5	NbBr_5	42
BBr_3	TaCl_5	TaBr_5	42
BBr_3	MoCl_5	MoBr_3	42
BBr_3	WCl_6	WBr_6	42
BBr_3	FeCl_3	FeBr_3	42
BBr_3	CoCl_2	CoBr_2	42
BBr_3	NiCl_2	NiBr_2	42
BBr_3	PtCl_4	PtBr_4	42
BBr_3	CuCl_2	CuBr_2	42
BBr_3	CdCl_2	CdBr_2	42
BI_3	SnCl_4	SnI_4	42
BI_3	SbCl_3	SbI_3	42
BI_3	TiCl_4	TiI_4	42

Traces of moisture and other impurities in boron systems which are usually air- and moisture-sensitive can affect the kinetics to a large extent¹¹⁷ while the thermodynamic picture is hardly changed. Consequently, much more rigorous conditions are needed for kinetic work.

Further interest in these systems arises from the use of boron trihalides as halogenating agents. Metathetical exchange reactions of boron trihalides with a variety of metal halides have been reported (see Table I). These exchange reactions may be generalized as in Eq. 4, and Eq. 5.

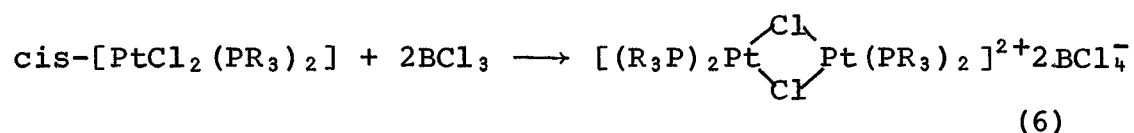


(X, Y = halogen, and X is heavier than Y)

Reactions of boron trihalides with metal halides may lead to, apart from halogen-exchanged products, three other types of complex. These are:

- (a) A Lewis acid-Lewis base adduct. The adducts of Group V_B halides with the boron halides¹¹³ are good examples.
- (b) A salt, with a tetrahalogenoborate anion. This situation is exemplified by the adduct SF₄,BF₃³³ which has the structure SF₃⁺BF₄⁻ (however, whilst SF₄ and BCl₃ exchange halogens, an intermediate has not been isolated).

(c) A halide-bridged cationic complex, and evidence for that is found in the formation of halide-bridged binuclear cationic platinum(II) complexes; e.g., reaction 6⁴³.



Lack of reaction (in an attempt to isolate complexes of types (a)-(c)) was observed⁴² (upon reflux) between BCl_3 and TiCl_4 , WCl_6 , and K_2PtCl_4 . Similarly, BBr_3 failed to react with SiCl_4 (300°/12h), GeCl_4 , $(\text{Pr}^n\text{BNCl})_3$, $(\text{PNCl}_2)_3$, Me_3SiCl^* , PSCl_3 , and K_2PtCl_4 . This may be because for these reactions there is no particular thermodynamic gain⁴². The behaviour of SiCl_4 and GeCl_4 is in contrast to other tetrahalides of Group IV, CCl_4 and SnCl_4 , which undergo exchange with boron trihalides¹⁰¹. (This work confirms the results observed for CCl_4 .) GeCl_4 , GeBr_4 , SnBr_4 , and SnI_4 had previously been shown not to form adducts with BBr_3 ². That PSCl_3 failed to react with BBr_3 , while $\text{BX}_3\text{-POX}_3$ 1:1 adducts are well known¹¹³, is consistent with the view¹¹³ that in the latter oxygen is the donor site. It had previously been observed that PSCl_3 does not react with BCl_3 ¹⁴⁰, although the exchange occurs with AlBr_3 ¹³⁷.

* Does not agree with my result (see p. 46).

It appears that exchange reactions of metal halides with boron tribromide and triiodide provide a convenient general method for the syntheses of anhydrous bromides and iodides, possibly the most widely useful of those currently available. By comparison with the oxide-BX₃ method^{42,83} yields are usually higher, a solvent may be employed, and the immediate product is often very pure without the necessity of further elaborate treatment. The last feature is particularly important for halides which are susceptible to decomposition during sublimation, e.g., FeBr₃. Further, reaction conditions are mild, pure starting materials are readily accessible, simple apparatus can be used, and separation of the boron by-product is not difficult. The method has been used by others in the actinide series²², and it is noteworthy that halogen exchange there is invariably more effective with boron trihalides than with silicon halides²². Likewise, BCl₃ was regarded as a more effective reagent than either CCl₄ or PCl₃ for the transformation of ReF₆ to ReCl₆²⁷; boron tribromide and ReF₆ afforded ReBr₅.

In general, BX₃ (X = Br or I) was regarded as a more effective reagent than CX₄, HX, SiX₄, or PX₃ as halogenating agents, or the reaction between metal and halogen, which generally requires vigorous reaction conditions^{26,32,68}. Knox, Tyree and their co-workers prepared some anhydrous chlorides using CCl₄^{81,100}; however, this method requires much more forceful conditions: ca. 400°, under pressure. The related reactions

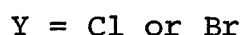
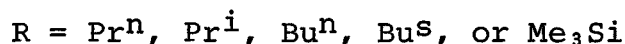
for bromides, using CBr_4 or other brominated hydrocarbons, are, however, not generally applicable, although uranium(IV) bromide has been obtained by this route¹¹⁶. Anhydrous metal chlorides have sometimes been prepared from oxides by use of non-metal chlorides, e.g., carbon tetrachloride, hexachlorobutadiene, carbonyl chloride, phosphorus(V) chloride, sulphur monochloride⁷⁹, thionyl chloride^{18,71}, octachlorocyclopentene⁹, aluminum trihalides^{28,54,124}.

Hartman and Schrobilgen⁶⁹ have found that the methylene halides CH_2Y_2 ($\text{Y} = \text{Cl}, \text{Br}, \text{I}$) tend to undergo halogen exchange with halogens other than fluorine when these are present either in tetrahaloborate anions or as halide ions. This has been found in studying the exchange reactions between mixtures of two (or three) tetrahaloborates which were examined by ^{19}F or ^{11}B NMR in CH_2X_2 solution. Dissociation of X^- from BX_4^- , followed by nucleophilic attack by halide ion X^- on CH_2Y_2 , is the most plausible mechanism for BX_4^- - CH_2Y_2 halogen exchange. Since bromide ion displaces chloride in CH_2Cl_2 only with difficulty, BBr_4^- is not expected to exchange halogen with methylene chloride to a significant extent⁶⁹.

Bowie and Musgrave¹⁷ have described the formation of organoboron compounds by the U.V. irradiation of mixtures of boron trihalides and aryl halides. Most of the products appeared to result from reactions of the aryl radicals formed by the photolysis of aryl halides, but some of the minor

products obtained from those reactions involving the less-easily photolysed aryl halides could not be accounted for in this way. Thus, boron tribromide and bromobenzene afforded, after hydrolysis, a little (3.2 %) p-bromophenylboronic acid while a similar reaction with chlorobenzene gave a somewhat larger yield (5.6 %) of p-chlorophenylboronic acid. They suggested that these products were formed by the photolysis of boron tribromide and reaction of the resulting dibromoboryl ($\text{Br}_2\dot{\text{B}}$) radicals with the excess of aryl halide present. This explanation was supported by their finding that the photolysis of a mixture of phenylboron dibromide and boron tribromide gave, after hydrolysis, a small (1.9 %) yield of p-phenylenediboronic acid¹⁷.

Goldstein et al.⁶⁵ have made a kinetic study of the halogen-exchange reactions of some of the halocarbon compounds with the complexed boron trihalide:

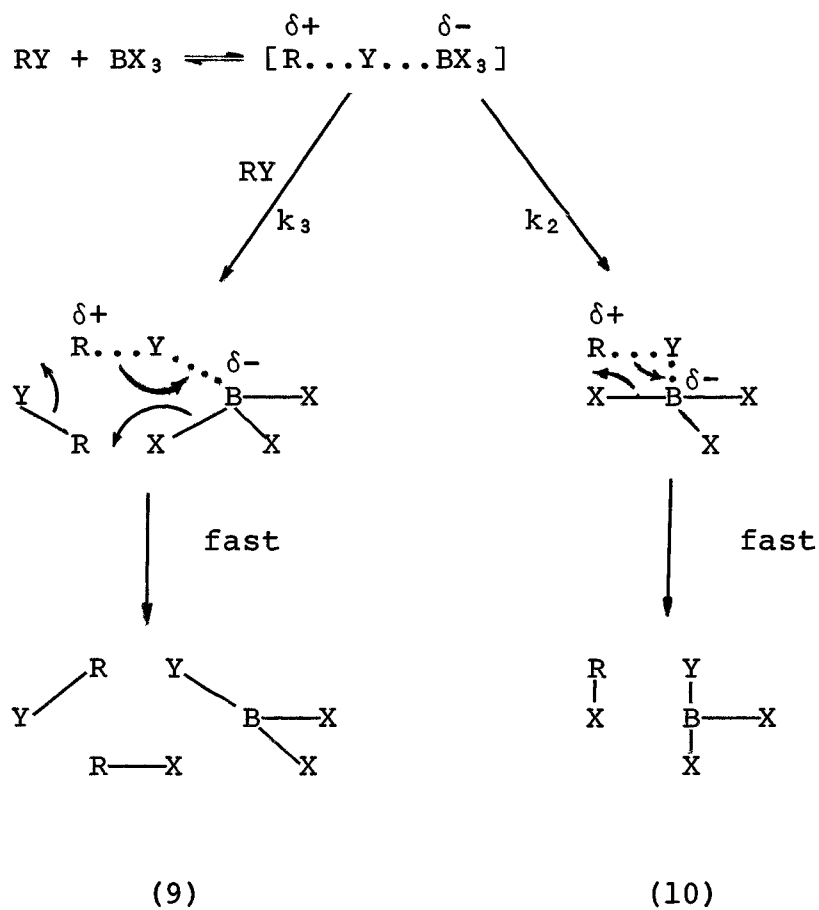


These reactions were found to occur only when X was heavier than Y^{61,111}, in cyclohexane or carbon tetrachloride at 306.5K by use of ¹H and ¹¹B NMR spectroscopy. For all these

reactions, the initial rate (r_0) depends on the initial concentrations of the reactants according to the relationship:

$$r_0 = k_3[\text{RY}]_0^2[\text{BX}_3]_0 + k_2[\text{RY}]_0[\text{BX}_3]_0 \quad (8)$$

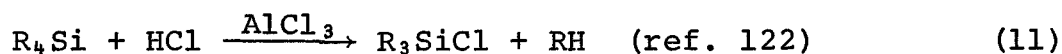
In most of the systems studied, the reactions are simply third-order (k_2 negligible), but cases showing second-order (k_3 negligible) or mixed--(second-plus-third)--order kinetics are found. Reactions of $\text{Bu}^{\text{S}}\text{Cl}$ with boron tribromide or boron triiodide are immeasurably fast, whereas those of $\text{Pr}^{\text{n}}\text{Cl}$ or $\text{Bu}^{\text{n}}\text{Cl}$ with boron tribromide are immeasurably slow under the conditions used. In all the aforementioned systems, the alkyl halide (RX) produced in the reactions showed no rearrangement compared with the starting compound (RY). However, during reactions of $(\text{Bu}^{\text{i}}\text{Y})$ with BX_3 ($\text{X} = \text{I}$ or Br), small amounts of $\text{Bu}^{\text{t}}\text{X}$ were formed. These reactions were found not to conform to any simple kinetic behaviour, and clearly involve several competing mechanisms. The temperature-dependence of the rate of reaction of $\text{Pr}^{\text{i}}\text{Cl}$ with boron tribromide (in carbon tetrachloride) has also been studied. Possible mechanisms for the reactions are suggested, requiring initial adduct formation of type $\text{RY} \cdot \text{BX}_3$ ⁶⁵



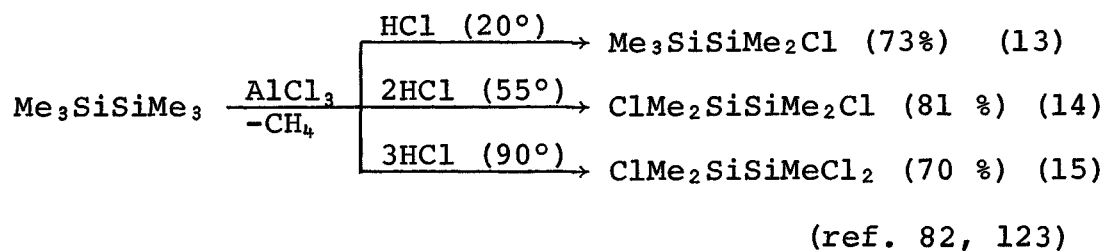
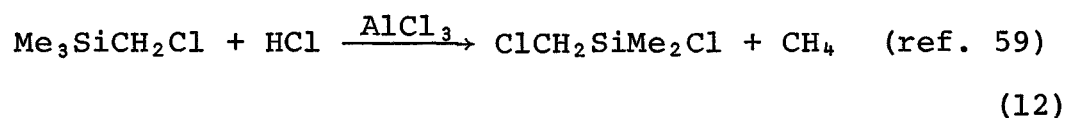
There were variations observed in the third-order rate constants with varying R, Y, and X. These can be rationalized at least in part by consideration of such factors as inductive effects of R, acceptor properties of BX_3 , polarizability of C-Y bonds, etc.

Part II

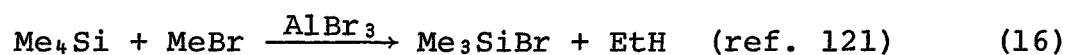
Cleavage of Si-C bonds by electrophilic reagents is known. Alkyl carbon-silicon bonds are very readily cleaved by hydrogen halides in the presence of aluminum halides, i.e., by the very strong acids HALX_4 ^{59,76,82,122,123} as illustrated below:



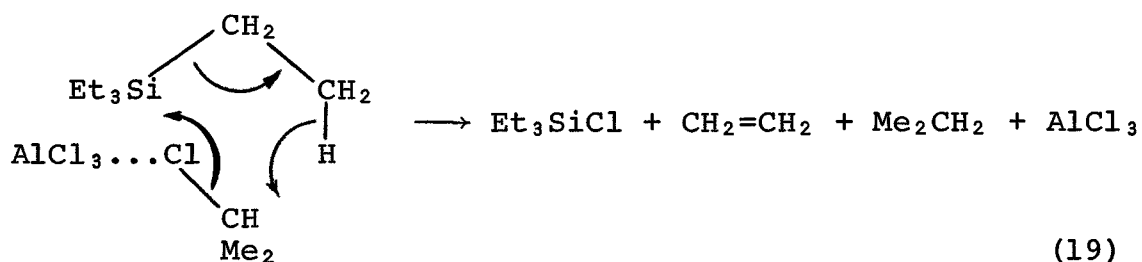
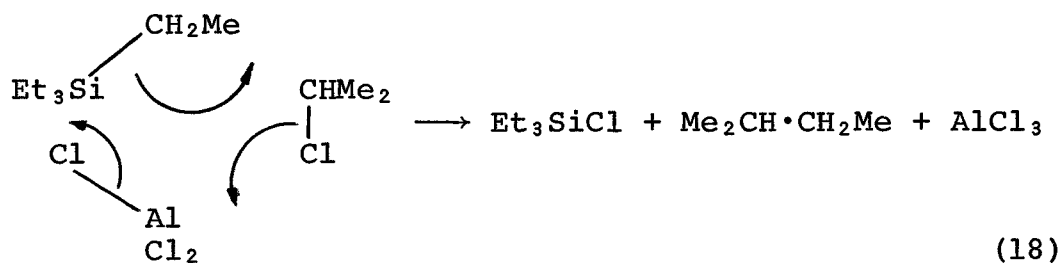
R = Me, Et



Cleavage of alkyl carbon-silicon bonds of tetraalkylsilanes and hexaalkyldisilanes is also brought about by alkyl halide-aluminum halide mixtures^{37,103,118,121,123,138,139} e.g.,



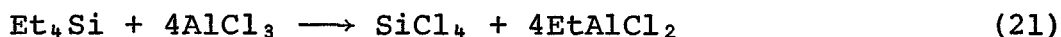
It has been suggested that two concurrent six-center processes are involved in the reaction with the tetraethylsilane^{138,139}:



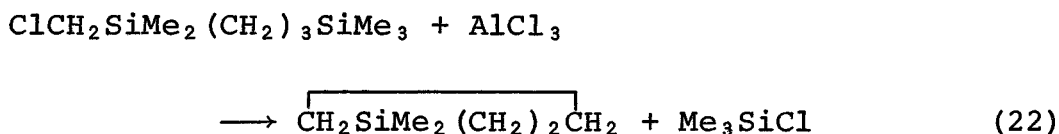
Cleavage of the alkyl carbon-silicon bond has also been noted in the reaction of bromine in ethyl bromide with Et_2SiCl_2 ¹¹. The mixed chlorobromosilanes, $\text{C}_2\text{H}_5\text{SiCl}_2\text{Br}$ and $\text{C}_2\text{H}_5\text{SiClBr}_2$ have been isolated in 53 and 30% yields respectively.



The cleavage of alkyl groups from silicon by aluminum halides alone has been reported^{93,121} e.g.,



The following cyclization¹⁰³ is also to be regarded as an example of this reaction:



It has been shown, however, that cleavage even of phenyl-silicon bonds does not occur under these conditions⁴⁴, and it is likely that the observed cleavages of alkyl-silicon bonds arose from the presence of moisture and/or hydrogen chloride, and thus of the acid HAlCl_4 . Also tetraethylsilane does not react with aluminum iodide in the presence of solvent⁴⁵.

Inorganic halides, other than aluminum trichloride⁹³, and aluminum tribromide¹²¹, such as FeCl_3 ^{93,121}, SbCl_5 ¹²¹, HgCl_2 ⁹⁴, GaCl_3 ^{125,126}, SnCl_4 ¹⁴³, and SbF_5 ¹⁰² have also been reported to cleave silicon-carbon bonds of alkylorgano-silanes with the subsequent formation of silicon-halogen bonds, although the reactions are generally not of preparative significance with respect to organohalosilanes. On the other hand, the transfer of an organic group (alkyl, alkenyl, alkylyl, aryl) from a metal in the same group of the Periodic Table as silicon to boron by the reaction of an organometallic reagent with an appropriate boron compound, is illustrated by examples shown in the following table:

TABLE II

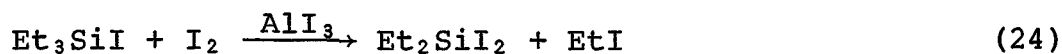
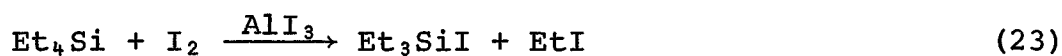
Transmetallation Reagent Combinations

Group X to be replaced by R in —B—X	Organometallic reagent ^a	Reference
Cl	R ₄ Si	14, 50
NR ₂	R ₄ Si	64
F	R ₄ Sn	20, 25, 29, 30, 120, 130
Cl	R ₄ Sn	5, 8, 20, 21, 24, 29, 30, 49, 52, 77, 78, 87, 104, 110, 130, 134
Br	R ₄ Sn	4, 55, 63, 77, 105, 110, 132
I	R ₄ Sn	107, 110, 127
H	R ₄ Pb	74
Cl	R ₄ Pb	73

^a R can be, variously, alkyl, alkenyl, or aryl in many, if not most, instances.

The cleavage of the silicon-carbon bond of tetraalkylsilanes by halogens has been investigated in detail. Chlorine and bromine halogenate the alkyl group without appreciable

cleavage, atomic mechanisms probably being involved⁴⁶; however, iodine in the presence of catalytic amounts of aluminum iodide causes cleavage⁴⁵ as shown below:



Further examples have also been studied in detail and gave similar results to the above mentioned ones^{31,44}.

Similar reactions involving boron trihalides have not been studied so far. It would be interesting to study the behaviour of such halides in comparison with the aluminum triiodide reactions. Similar behaviour would naturally be expected of boron halides and aluminum halides since they both belong to the same group in the Periodic Table. It was therefore deemed useful to study the reactions of some alkyl silicon compounds with boron triiodide and boron tribromide.

EXPERIMENTAL

EXPERIMENTAL

General Techniques

A glove-bag was used as a convenient device for the handling, transfer, filtration and preparation of NMR samples of moisture- or air-sensitive materials in an inert atmosphere. It was capable of providing an extremely clean atmosphere, especially when the nitrogen was circulated through a purification line of calcium chloride and phosphorus pentoxide mixed with glass wool.

Schlenk techniques were used in some experiments under an atmosphere of dry N_2 . Rubber septa and hypodermic needles were a convenient method for transferring a liquid to or from a vessel without introducing air.

All glassware and NMR tubes which were used had been baked overnight in an oven at ca. $110^\circ C$ and finally purged, while hot, with a stream of dry nitrogen.

Chemicals that were reactive towards rubber stoppers and/or greased stopcocks were stored in special vials (Fig. 1) stoppered with Mininert valves, NO SC-20. The same vials were used as reaction vessels for exchange reactions which required long periods of time.

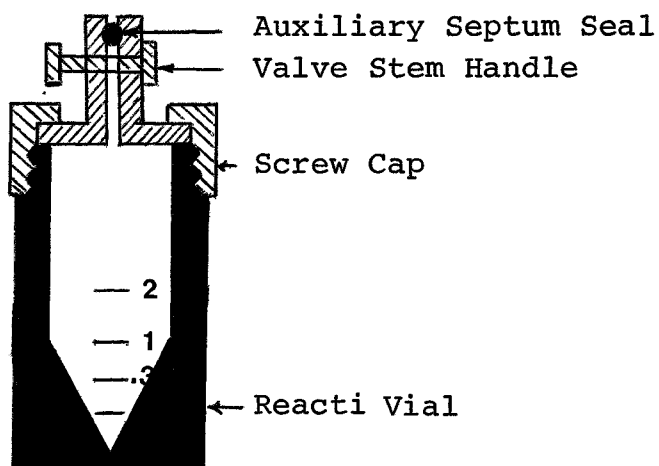


Fig. 1. Mininert valves for Screw-cap Bottles

Purification of Reagents

Boron triiodide

The instability of boron triiodide is well known; it decomposes even in the solid state to iodine and unspecified boron polymers⁷⁵. Boron triiodide was dissolved in carbon disulfide and shaken with mercury. After filtration, using Schlenk techniques, carbon disulfide was removed in vacuo (20°C/0.1 mm Hg), leaving almost white crystals of the triiodide.

Boron tribromide

Boron tribromide was purified by treatment with mercury (to remove any bromine), heating under reflux (to remove any hydrogen bromide), and distillation (b.p. 90°). Carbon disulfide was dried over phosphorus pentoxide and distilled therefrom.

Boron trichloride and trifluoride were used without further purification.

1,1,1-Trichlorethane was freed from its stabilizer (dioxane) by washing several times with water and drying over Molecular Sieves, 5Å.

All other reagents were purified, dried, and distilled by appropriate methods where necessary by fractional distillation (for liquids) or recrystallization and vacuum sublimation (for solids). Purity of volatile substances was checked by GC/MS techniques.

Reagents obtained from suppliers are listed in Table III.

Instrumentation

Proton (Nuclear) Magnetic Resonance Spectra

PMR data were recorded with a Varian A-60 NMR spectrometer operating at a fixed frequency of 60 MHz. Tetramethylsilane (TMS) dissolved in deuterated chloroform (1% v/v) was used as an internal reference standard ($\delta = 0$ Hz). TMS was added just before taking the spectrum to avoid any side reaction as a result of reacting TMS with excess boron halides. Chemical

TABLE III

REAGENTS

Compound	Formula	Supplier
Boron triiodide	BI_3	Alfa Inorganic, Ventron, Beverly, Massachusetts, U. S. A.
Boron tribromide	BBr_3	Alfa Inorganic
Boron trichloride	BCl_3	Matheson of Canada, Whitby, Ontario
Boron trifluoride	BF_3	Matheson of Canada
TMS	$(CH_3)_4Si$	Merck Sharp & Dohme of Canada Limited, Montreal, Canada
Hexamethyldisilane	$(CH_3)_6Si_2$	NMR Specialties Incorporated 1410 Greensburg Road, New Kensington, Pennsylvania U. S. A. 15068
Hexamethyldisiloxane	$(CH_3)_6Si_2O$	NMR Specialties
Chlorotrimethylsilane	Me_3SiCl	Aldrich Chemical Company, Inc.
Dichlorodimethylsilane	Me_2SiCl_2	Aldrich Chemical Company, Inc.
2,2-Dimethylbutane	$CH_3CH_2C(CH_3)_3$	Aldrich Chemical Company, Inc.
Chloroform-d	$CDCl_3$	Merck Sharp & Dohme Canada Ltd.
Chloroform	$CHCl_3$	Merck Sharp & Dohme Canada Ltd.
Bromoform	$CHBr_3$	Chemical Service Media, Pennsylvania, U. S. A.
Fluorotribromomethane	$CFBr_3$	PCR, P.O. Box 1466, Gainesville, Florida, U. S. A. 32602
Fluorotrichloromethane	$CFCl_3$	K & K Laboratories, Inc. Plainsview, New York, U.S.A.
Bromotrichloromethane	$CBrCl_3$	Aldrich Chemical Company, Inc.

Table III, continued

Compound	Formula	Supplier
1,1,1-Trichloroethane	CH_3CCl_3	J. T. Baker Chemical Co. Phillipsburg, New Jersey U. S. A. 08865
1,2-Dichloroethane	$\text{Cl}(\text{CH}_2)_2\text{Cl}$	Fisher Scientific Company
2-Chlorobutane	$\text{CH}_3\text{CHClCH}_2\text{CH}_3$	BDH Chemical Limited, Poole, England.
α,α,α -Trichlorotoluene	$\text{C}_6\text{H}_5\text{CCl}_3$	Chemical Service, Media, Pennsylvania.
1,1-Bis (p-chlorophenyl) - 2,2,2-trichloroethane (P,P'-DDT)	$(\text{ClC}_6\text{H}_4)_2\text{CHCCl}_3$	Aldrich Chemical Company, Inc.

shifts downfield from TMS were reported in ppm and Hz to an accuracy of ± 0.5 Hz.

Some of the NMR data were recorded with a Bruker WP-60 FT-NMR tuned for protons at 60.00 MHz. Samples were run using both internal and external locks (in capillary tubes). Chemical shifts were either read directly from the computer listing or calculated from the calibrated plots to an accuracy of ± 0.3 Hz.

Combined Gas Chromatography and Mass Spectrometry.

The technique of combined gas chromatography and mass spectrometry seemed to work very well for analysis of the reaction products. Most of this work was done using a Pye-Unicam 104 gas chromatograph interfaced to an AEI-MS-30 double beam, double focusing mass spectrometer through both a silicone membrane separator and a glass Bieman frit separator. The ionization voltage was 70 eV; accelerating voltage, 4 KV; resolution, ca. 1000; filament current, 100 μ amps; source temperature, 200°C; separator temperature, 250°C; connecting line temperature, 250°C; column temperature, programmed linearly from 25° to 180° at 20°C/min; and a helium flow rate of 40 ml/min. PFK (perfluorokerosene) was used as a mass marker.

The initial gas chromatograms were recorded on an F and M 700 model gas chromatograph which is equipped with a thermal conductivity detector. This instrument had a dual column, the use of which compensates for any substrate bleed

at high temperatures. It was interfaced to an F and M model 240 power proportioning temperature programmer. The carrier gas used was helium. SE30 was used as the liquid phase and Chromosorb W was used as the solid support. A uniform coating of SE30 (5%) on Chromosorb W was made by slowly adding Chromosorb W to a solution of SE30 in methylene chloride while the solution was kept stirred. Finally the methylene chloride was removed on a rotary evaporator. A 3-foot teflon column was packed with the above material and conditioned overnight while helium was passed through it. Then the column temperature was programmed suitably and the flow rate was adjusted to 40 ml/min. The injector temperature was 180°. Five microlitres of the reaction product was injected into the injection port.

Preparation of the Sample

The reaction vessel in most of the cases was a 5 mm outside diameter NMR tube provided with a rubber septum. As boron halides react with rubber, special vials with Mininert valves were used for exchange reactions that required long times. Calculated quantities of boron halide and organic compound (e.g., 1:1 mole ratio) were placed in clean dry NMR tubes. The liquid samples were transferred to the NMR tubes by means of a hypodermic syringe through the septum. Reactions were carried out by heating the bottom portion of the NMR tube in an oil bath while the top portion was kept cooled. The reaction was monitored by PMR.

On completion of the exchange reactions, the samples for product determination were prepared by two methods. In the first, the excess of boron trihalide was complexed with pyridine and the solid adduct was filtered off. The filtrate was examined by GC/MS. This method left some free iodine in the source of the mass spectrometer and was therefore not very satisfactory. In the second method the excess of iodine was destroyed by sodium thiosulfate and the unreacted boron trihalide was hydrolysed. There was no significant difference between these results and those obtained by adding pyridine, although the latter reacts vigorously with boron halide, and accordingly causes a partial decomposition of the reaction products. The separation of the products of the reactions between boron trihalide and carbon-silicon compounds on the gas chromatograph was unsuccessful as the products appeared to decompose in the column whereas in that of the boron halide/carbon-halide system, partial decomposition of some products led to peaks in the latter part of the chromatogram.

RESULTS AND DISCUSSION

Results and Discussion

Part I

In this work a number of different alkyl and aryl halides have been subjected to reaction with boron triiodide and boron tribromide. Generally most of them have undergone stepwise halogen exchange resulting in the final product where all the original halogens were replaced by the halogen from the boron trihalide. The reaction rates were different for different types of the organic compounds. The reactions were generally conducted by mixing the organic liquid (or a solution of the organic solid) with boron trihalide at room temperature or refluxing for a few hours. Exchange reactions between organic halides and boron halides studied are summarized in Table IV.

The reactions were monitored by either ^1H N.M.R. or GC/MS techniques or both. Boron triiodide is more reactive than boron tribromide and exchange reactions are often relatively rapid. The high reactivity of boron triiodide sometimes causes decomposition when reactive organic halides are used, e.g., α,α,α -trichlorotoluene and DDT. In these cases, solvents were used to dilute the organic compound and consequently to minimize the thermal decomposition of boron triiodide to iodine and polymeric boron compounds.

TABLE IV. Exchange Reactions Between Organic Halides and Boron Halides

Reactants	Conditions	Time	Products of the Reaction		Detection Method
			Exchange Products	Other Products	
CCl_4	BI_3 25°	5 weeks	$\text{CClI}_3^\bullet, \text{CI}_4^{a*}$	$\text{C}_2\text{I}_4^0, \text{CHI}_3^0, \text{CH}_2\text{I}_2^\bullet$	GC/MS
CCl_4	BBr_3 25°	5 weeks	CBr_4^*	CHBr_3°	GC/MS
CBr_4	BI_3 Benzene, 25°	5 weeks	CI_4^*	CHI_3°	GC/MS
CHCl_3	BI_3 25°	5 weeks	CHI_3	--	GC/MS
CDCl_3	BI_3 25°	5 weeks	$\text{CDICl}_2^\bullet, \text{CDI}_2\text{Cl}^\bullet, \text{CDI}_3^*$	--	GC/MS
CHCl_3	BBr_3 25°	7 weeks	CHBr_3	--	GC/MS
CHBr_3	BI_3 25°	7 weeks	CHI_3	--	GC/MS
CBrCl_3	BI_3 25°	12 days	--	CHI_3	GC/MS
CFCl_3	BI_3 25°	5 weeks	NO EXCHANGE		$^1\text{H NMR}$ GC/MS
CFBr_3	BI_3 25°	7 weeks	$\text{CFBr}_2\text{I}^\bullet$	$\text{CHBr}_3^\circ, \text{CHI}_3^*$	GC/MS
CH_2Cl_2	BI_3 25°	12 days	$\text{CH}_2\text{ICl}^\bullet, \text{CH}_2\text{I}_2^*$	--	GC/MS
CD_2Cl_2	BI_3 25°	12 days	$\text{CD}_2\text{ICl}^\bullet, \text{CD}_2\text{I}_2^*$	--	GC/MS

Table IV continued, p. 3

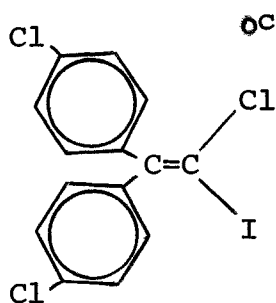
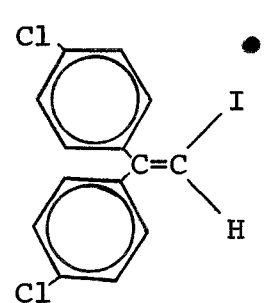
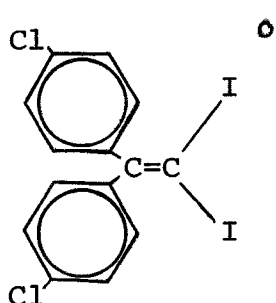
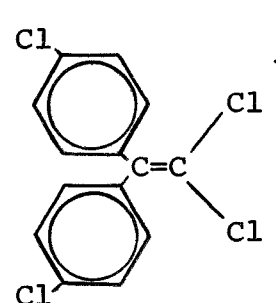
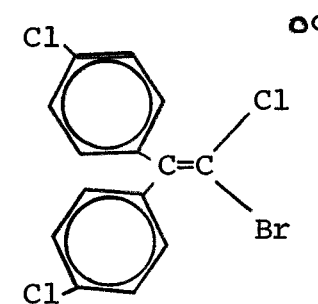
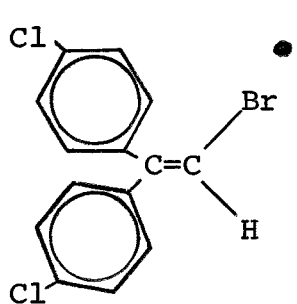
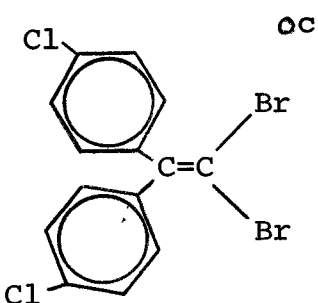
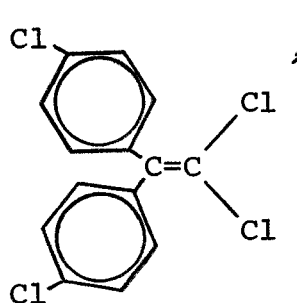
Reactants	Conditions	Time	Products of the Reaction		Detection Method
			Exchange Products	Other Products	
P,P'-DDT	BI ₃ CCl ₄ , 70°	48 hours			¹ H NMR GC/MS
					
$\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{CH}_3$	BBr ₃ 70°	12 hours	$\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$	--	¹ H NMR GC/MS
ClCH ₂ CH ₂ Cl	BBr ₃ 80°	48 hours	NO EXCHANGE		¹ H NMR GC/MS

Table IV continued, p. 4

Reactants	Conditions	Time	Products of the Reaction		Detection Method
			Exchange Products	Other Products	
P,P'=DDT	BBr ₃ CCl ₄ , 70°	48 hours			¹ H NMR GC/MS
					

^a CCl₄ is relatively unstable, it decomposes to C₂Cl₄ + I₂ or it very easily picks up a hydrogen atom from any source (e.g., rubber septa) to give the more stable compound CHI₃.

^b These compounds are due to dehydrohalogenation of some of the products in the column. Other compounds could be due to the thermal decomposition of initial products and obviously the former were not shown in the NMR analysis.

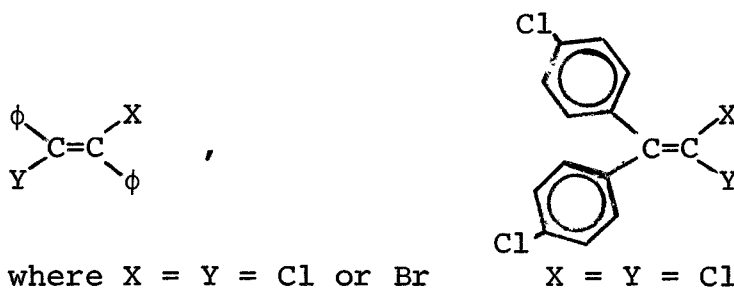
^c Exchange accompanied by HX (X = Cl, Br or I) evolution. No DDT left after 5 hours.

* Major product

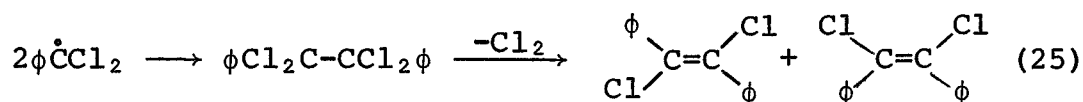
o Minor product

• Trace product.

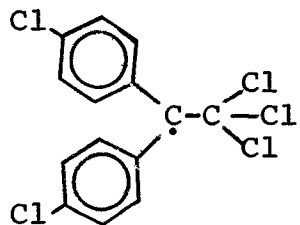
The reactions appear to proceed by either an ionic or a radical mechanism or a combination of both. Without a full kinetic study it is impossible to assign a specific mechanism for the halogen exchange in these reactions, but one thing is evident: the reaction between α,α,α -trichlorotoluene or DDT and boron halide proceeded by a combination of both ionic and radical mechanisms. This is proved by the formation of the products



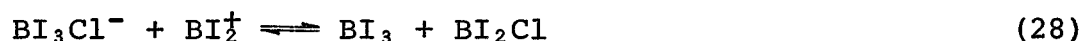
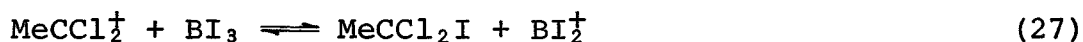
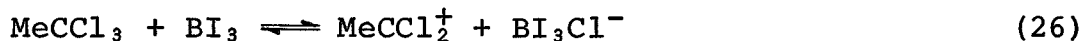
in those reactions. The former might be derived from the compound formed from the coupling of 2 $\phi\dot{\text{C}}\text{Cl}_2$ radicals, accompanied by dehalogenation.



The latter is likely to be formed from the stable radical



Exchange of substituents could occur by more than one possible mechanism. 1,1,1-Trichloroethane is taken as an example. Halogen exchange could occur by ionic mechanism as follows:

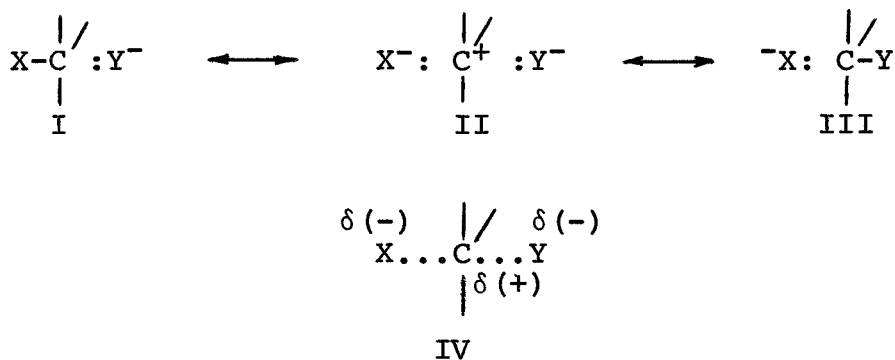


etc.

An additional possible mechanism is by a nucleophilic (S_N2) attack of I^- on MeCCl_3 . I^- could exist as a result of a preliminary dissociation of one of the ligands of the tetrahedral boron compounds such as BI_3Cl^- (Eqns 26, 28), as shown in Eqn. (29).



The reaction mechanism may then be considered in terms of the structure of the transition state configuration, which may be regarded as a resonance hybrid of structures I, II, and III¹⁴². The hybrid structure may be written as IV, in which the dotted lines represent partial covalent bonds with the charge distribution as indicated.



Alternatively, the transition state may be examined from a molecular orbital viewpoint and the structure written as in Figure 2. To arrive at this structure, a rehybridization of the four original sp^3 orbitals of the central carbon must take place.

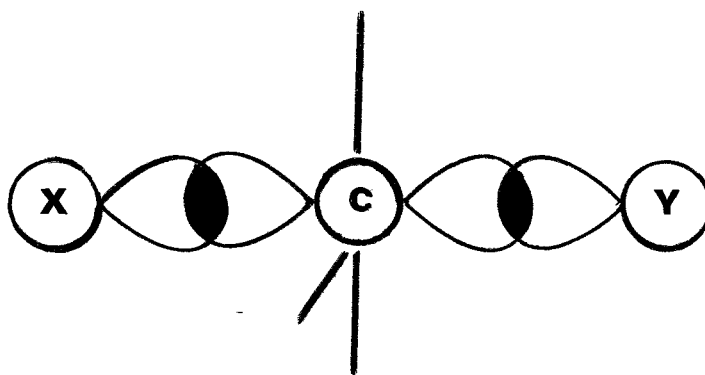
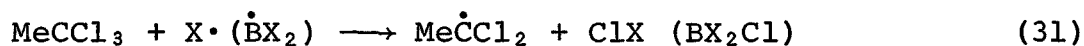


Figure 2. An orbital representation of the transition state of a direct displacement reaction.

The three bonds not undergoing reaction are coplanar and are made up of three sp^2 orbitals of the central carbon. The remaining p orbital, perpendicular to the plane of the other three orbitals, and an orbital of both the entering and the

leaving group combine in the manner shown in Figure 1 to form a set of molecular orbitals. In the usual LCAO approximation, three molecular orbitals will be formed, two of which, a bonding and a nonbonding orbital, will contain the total of four electrons available. Since atoms X and Y are generally effectively more electronegative than carbon, the central carbon atom will be partially electron-deficient.

Another possible mechanism to explain the formation of these products is the photolysis or thermolysis of the boron trihalide and the reaction of the resulting halide (X^*) radicals with the excess of organic halide present as follows:



Despite a careful search, we were unable to obtain any of the $MeCCl_2$ from either reaction ($X = I$ or Br). This suggests that

the steric effects of the $-BBr_2$ and $-BI_2$ groups hinder substitution on the central carbon atom.

Another possible mechanism for this type of reaction involves the initial adduct formation of type $RY \cdot BX_3$,⁶⁵ followed by its decomposition to the products through either a four-centre or six-centre transition state as shown in Scheme II.

SCHEME II

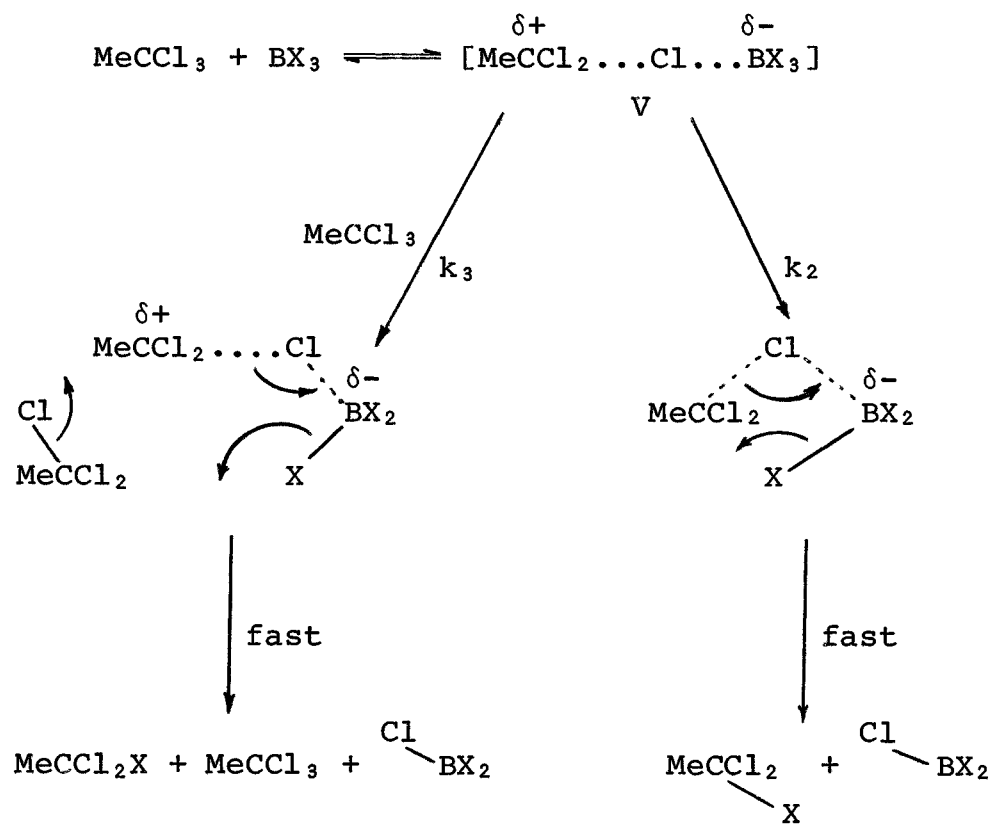


TABLE V. Chemical shifts of MeCX_3 , MeCX_2Y and MeCXY_2 in ppm.

Compound	ppm	
MeCCl_3	2.73	(2.73) ^a
MeCBr_3	3.40	
MeCI_3	4.44	
MeCCl_2Br	2.91	
MeCCl_2I	3.14	
MeCClBr_2	3.13	
MeCClI_2	3.72	

^a Reference 99a.

In this system, MeCHXY (see Table VI for the chemical shifts) was also formed.

TABLE VI. ^1H Chemical shifts of CH_3CHXY in ppm

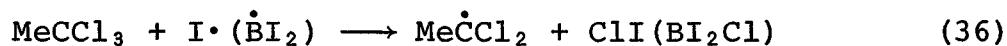
X	Y	$-\text{CH}_3$		$-\overset{ }{\text{C}}\text{H}-$		J cps, Obs.	$-\text{CH}_3, -\overset{ }{\text{C}}\text{H}-$	
		Obs.	Lit. ^a	Obs.	Lit. ^a		Obs.	Lit. ^a
I	I	2.93	2.96	5.18	5.23	7.0	7	
I	Cl	2.48	2.49	5.90	5.90	6.5	6.5	
Cl	Cl	2.08	2.02	5.84	5.89	6.0	6.0	

^a Reference 104a.

This might be due to the presence of H-containing compounds (e.g., rubber septum, traces of water) in the system. An experiment was carried out in which a sample of MeCCl_3 wetted with D_2O was reacted with BI_3 . It showed a triplet for the methyl group with a coupling constant of 1 Hz. This is

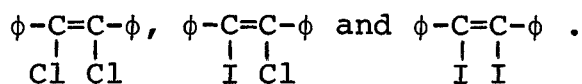
obviously due to CH_3CDCl_2 .

The following mechanism would also explain the formation of the side product:

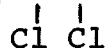


HR could be rubber or any organic material

When boron triiodide and α,α,α -trichlorotoluene in carbon tetrachloride (used as solvent) were mixed in a 1:1 mole ratio and the mixture allowed to warm to room temperature in an N.M.R. tube, a vigorous reaction occurred. The N.M.R. tube was warmed in an oil bath for the completion of the reaction. An attempt to separate the products of the reaction by fractional distillation was unsuccessful. Gas chromatographic analysis combined with mass spectral analysis identified the following components:



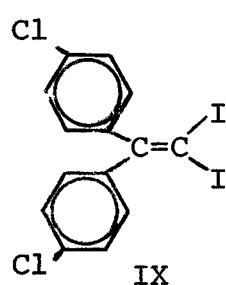
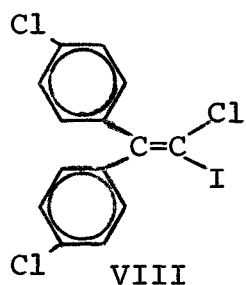
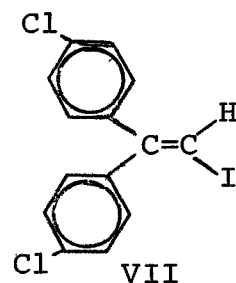
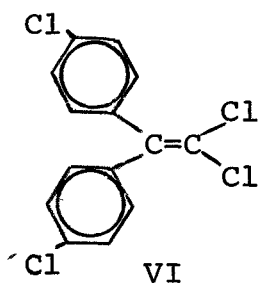
All the above compounds except the last three are products of halogen exchange and in some cases abstraction of H-atom by radical intermediates. The last three are obviously products derived by coupling of radicals followed by dehalogenation of these products. $\phi-\text{C}=\text{C}-\phi$ was the major component compared to



the other two. Therefore it may be reasonable to assume that

halogen exchange is less favoured once the halogen is bonded to the sp^2 hybridized carbon atom. Further work in this line with olefinic compounds containing halogen atoms is indicated. Reaction of boron tribromide with α,α,α -trichlorotoluene showed similar results.

DDT in carbon tetrachloride was allowed to react with boron triiodide (1:1 mole ratio). The reaction was completed by warming the N.M.R. tube in an oil bath for 48 hours at 70° . The singlet at $\delta = 5.03$ ppm due to the aliphatic proton of the DDT had completely disappeared in the ^1H N.M.R. at the end of the reaction. The products detected by GC/MS were VI, VII, VIII and IX. VI was the major product.



All the above products were formed by the dehydrohalogenation of DDT. The formation of such compounds can be favoured due to the fact that the two aromatic rings are in conjugation with the newly formed double bond. There are two possible ways by which the double bond could be formed; in one case by the removal of HCl and the other by the removal of HI. In this case it is difficult to predict which of the two pathways was followed, although there is a greater possibility of the halogen exchange occurring first followed by the dehydrohalogenation.

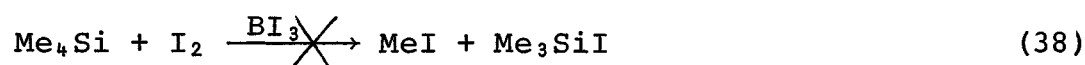
Part II

This table summarizes all the reactions between boron halide and organo-silicon compounds used.

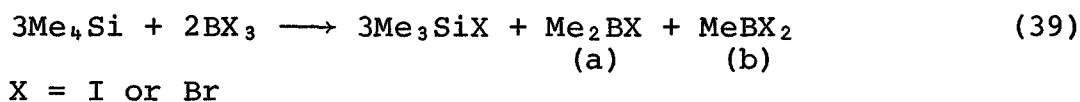
Reactants	Conditions	Time	Products of the Reactions*	
Me ₄ Si	BX ₃ X = Br, I	28°	1 hour	Me ₃ SiX, Me ₂ BX, MeBX ₂
Me ₃ SiSiMe ₃	BX ₃ X = Br, I	70°	1 hour	Me ₃ SiSiMe ₂ X, XMe ₂ SiSiMe ₂ X, MeBX ₂
Me ₃ SiCl	BX ₃ X = Br, I	25°	2 weeks	Me ₃ SiX, BX ₂ Cl
Me ₂ SiCl ₂	BX ₃ X = Br, I	70°	4 hours	Me ₂ SiClX, Me ₂ SiX ₂ , BX _n Cl _{3-n} (n=0,1,2,3)
(Me ₃ Si) ₂ O	BX ₃ X = F, Cl, Br, I	25°	4 hours	Me ₃ SiX, B ₂ O ₃

* Detection method used was ¹H NMR

In the reaction of tetramethyl silane, iodine and boron triiodide, the latter did not act as a catalyst because no methyl iodide had been detected in the products. MeI should be a product if BI_3 acts as a catalyst^{4 5}



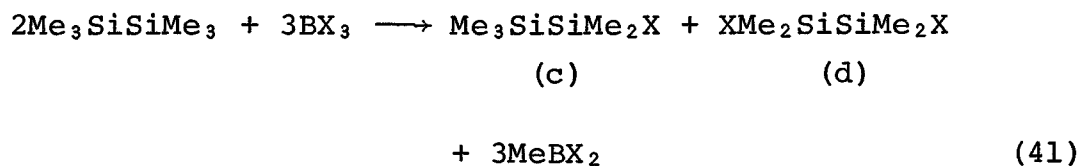
The silicon-carbon bond is easily cleaved on refluxing tetramethyl silane with boron triiodide or boron tribromide.



Actually compound (b) is detected only in trace amounts in the mixture, however, on adding excess of boron halide, compound (b) increased significantly due to the transformation of (a) to (b) as illustrated in the following equation

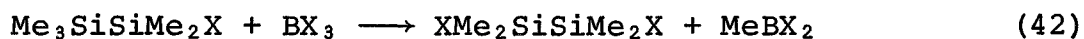


Similar results were obtained in using hexamethyldisilane instead of TMS.

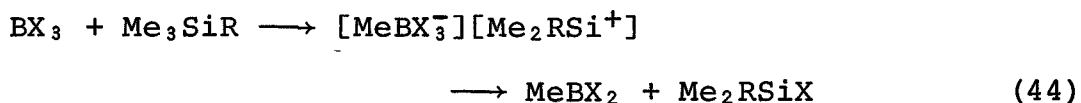
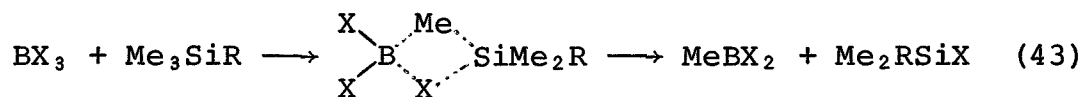


X = I or Br

Also, on adding an excess of boron halide, compound (c) is converted to compound (d) as shown in Eqn. (42).



There are at least two possible mechanisms to explain the transfer of organic groups from silicon to boron¹¹², Eqns. (43) and (44).



R = Me or SiMe₃

X = I or Br

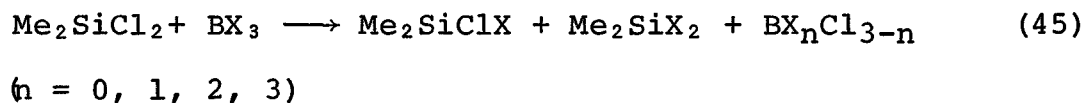
Obviously, Eqn. (43) should be favoured with less polar solvents (or absence of solvent).

The second-order pathway is more likely to involve the four-centre transition state shown in equation (43) than formation of $[\text{MeBX}_3]^-[\text{Me}_2\text{RSi}]^+$ because:

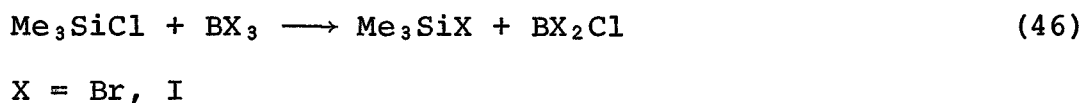
- (i) the solvent used is of low polarity or no solvent used at all,
- (ii) isomerization was not observed,
- (iii) the available evidence^{3,99,121} is against the formation of siliconium ions in solution, and
- (iv) intermediates of this type have been frequently suggested in many redistribution reactions¹¹²

The possibility of second methyl-silicon bond cleavage and of introducing a second iodine atom is decreased. The increasing electron-withdrawal from the silicon atom, and thus from the methyl group, as an additional iodine atom is attached to silicon lowers the ease of electrophilic attack at the methyl group. Consequently the methyl groups will become unable to participate again in a transition state similar to the one in Eqns. (43) and (44), and the second methyl-silicon bond is not cleaved.

A separate experiment was done to prove the above explanation. In the case of reaction of dimethyl-dichlorosilane with boron triiodide or boron tribromide, there was halogen exchange instead of silicon-carbon cleavage as expected:



Druce and Lappert⁴² have attempted halogen exchange on trimethylchlorosilane, using boron tribromide, under conditions of prolonged reflux, but without success. However, when the same compound was reacted at room temperature with boron tribromide or boron triiodide for two weeks, the corresponding trimethylsilane halides were obtained and confirmed by comparing their chemical shifts with the literature data^{48, 51, 136}.



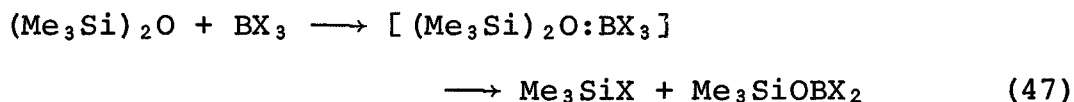
Similar results have been obtained by Hartman and Schrobilgen⁶⁹, on reacting BF_4^- with $(\text{CH}_3)_3\text{SiY}$ (Y = halogen) the halogen exchange occurred and $(\text{CH}_3)_3\text{SiF}$ was found.

It would appear reasonable to attribute this effect to the strong electron donating power of a halogen as compared with a methyl group, into the empty p-orbital of the boron atom, thus favouring halogen exchange over carbon-silicon bond cleavage.

Features favouring the exchange process include the greater volatility of boron trichloride than boron tribromide and boron triiodide, the higher Lewis acidity of boron triiodide than boron tribromide and boron trichloride, and the

possible favourable enthalpy change (i.e., in simplified form that $\bar{E}(\text{C-B}) + \bar{E}(\text{Si-I})$ is greater than $\bar{E}(\text{B-I}) + \bar{E}(\text{Si-C})$). Lack of reaction was observed in an attempt to react boron triiodide or boron tribromide with Me_3CEt ($80^\circ/24$ h). This may be because for this reaction there is no particular thermodynamic gain. Thus, for example (data from ref 38): $\bar{E}(\text{C-C}) + \bar{E}(\text{B-Br}) = 82.6 + 90 = 172.6 \text{ kcal mol}^{-1}$, whereas $\bar{E}(\text{C-Br}) + \bar{E}(\text{B-C}) = 68 + 89 = 157 \text{ kcal mol}^{-1}$. On the other hand the C-C bond is stronger than the Si-C bond (83 vs 76 kcal mol^{-1}), and the latter is weak enough to be broken. This is in turn caused by the larger size of the silicon atom so that the Si-C bond must be longer and the electrostatic force holding the atoms together correspondingly weaker.

Another experiment has been done to prove the above assumption. On reacting a boron trihalide with hexamethyldisiloxane, cleavage of the Si-O-Si bond occurs with formation of the methylhalogenosilane and the methylsiloxyboron dihalide. The latter decomposes spontaneously to the methylhalogenosilane, boron trihalide and the boron trioxide.



X = F, Cl, Br, I

The composition of the residue left after hydrolysis of the products from the reaction between hexamethyldisiloxane and boron halide was established as follows:

A flame test of the sample proved the presence of boron (green flame), the solid melted at a very high temperature (ca. 450°). A sample of the white solid was accurately weighed and titrated against standard sodium hydroxide in the presence of excess glycerol following Thomas' method¹³³. The analytical results were as follows:

Molarity of sodium hydroxide = 0.0952 M

Weight of residue (B_2O_3) = 0.0200 g

Volume of sodium hydroxide consumed = 6.00 ml

Boron calculated = 31.06% (for B_2O_3)

Boron found = 30.98%

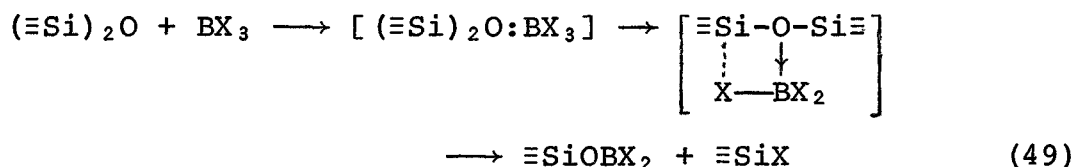
This proved the composition of the residue to be B_2O_3 .

The results showed that, unlike the alkyl ethers, the disilyl analogues did not form a stable 1:1 addition compound with boron trihalide. Instead, cleavage of the Si-O-Si bond occurred. The stability of the methylsiloxyboron dihalide formed decreases with decreasing Lewis acidity of the boron halide ($BI_3 > BBr_3 > BCl_3 > BF_3$).

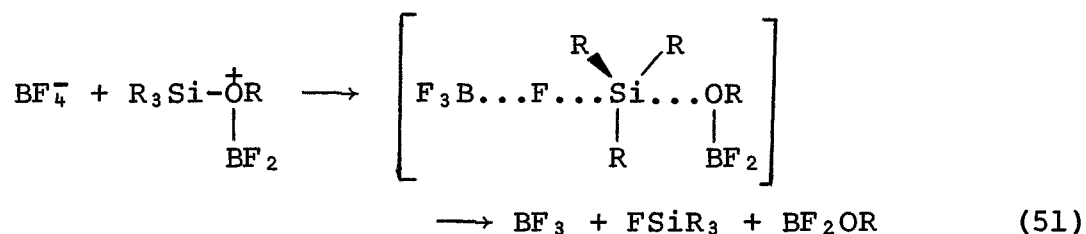
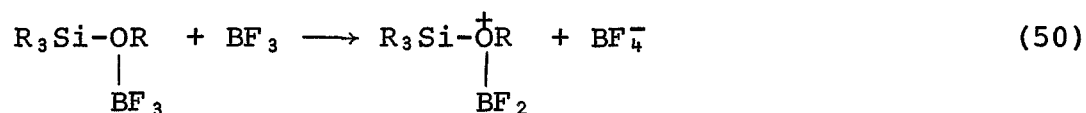
The failure of hexamethyldisiloxane to form a stable coordination complex supports the current theoretical view of the ability of silicon to use its vacant 3d-orbitals in the

formation of π -type bonds with oxygen which have considerable double-bond character. For boron trihalide, the possible formation of adducts of low stability is masked by halogenation in which silicon-oxygen bonds are broken. This occurs more readily than the cleavage of carbon-oxygen bonds in either and the former is favoured by the larger size of the silicon atom, which favours polar attack, and also by the fact that the silicon-oxygen bond is more polar than the carbon-oxygen bond.

The mechanism which has been proposed for the reaction of alkyl ethers with boron halides involves an electrophilic attack by boron halides, with transitory formation of a carbonium cation^{60,62}. Organosilicon compounds do not form siliconium¹³¹ and a similar mechanism is therefore unlikely in the reactions of disiloxanes with boron halides. Instead, the mechanism proposed for the cleavage of the siloxane linkage by boron halides involves the initial formation of an acid-base adduct, which irreversibly decomposes with cleavage of the silicon-oxygen bond through a simple four-centre mechanism:



Another mechanism has been proposed¹²⁹, which gives an explanation for the inversion of configuration in some cases. The cleavages of alkoxysilanes with boron trifluoride or the boron trifluoride etherate proceed with a definite inversion of configuration. The inversion mechanism proposed involves a S_N2 -silicon attack of a fluoride ion (or a complexed fluoride ion in the nonpolar solvents used) at the rear of silicon displacing the alkoxy group, the leaving ability of which has been enhanced by coordination¹²⁹, i.e.,



The difference in mechanisms for the two boron halide cleavage reactions may be due, in part, to the relative Lewis acidities of boron trifluoride, boron trichloride, boron tribromide and boron triiodide. Boron trichloride, for example, is a stronger acid than boron trifluoride, hence the silicon-oxygen bond should be weakened more on coordination with boron trichloride than with boron trifluoride. This should then make the silicon site in the boron trichloride complex more receptive to accepting a chloride ion intermolecularly via the four-centre mechanism than it would to a fluoride ion¹²⁹.

Supporting data:

1. Nuclear Magnetic Resonance Spectra

Tables VII and VIII summarize all the chemical shifts obtained for each compound in deuterated chloroform or benzene as solvent.

Table VII. ^1H N.M.R. chemical shifts data (δ in ppm) for some derivatives of methylsilane

Compound	CDCl_3 (20%)	C_6H_6 (20%)
Me_3SiF	0.217 ^a (0.17 ^d , 0.21 ^e 0.20 ^f)	
Me_3SiCl	0.38 (0.37 ^d , 0.42 ^f)	0.18 (0.18 ^b , 0.23 ^c)
Me_3SiBr	0.57 (0.51 ^d)	0.35 (0.36 ^c)
Me_3SiI	0.80 (0.73 ^d)	0.533 (0.53 ^c)
Me_2SiCl_2	0.76 (0.8 ^f)	0.35 (0.35 ^b , 0.43 ^c)
Me_2SiBr_2	1.04	0.71 (0.72 ^c)
Me_2SiI_2	1.53	1.08 (1.09 ^c)
Me_2SiClBr	0.89	
Me_2SiClI	1.12	0.68
$\text{Me}_3\text{SiSiMe}_2\text{Br}$	0.17, 0.6	0.07, 0.33
$\text{Me}_3\text{SiSiMe}_2\text{I}$	0.22, 0.87	
$\text{BrMe}_2\text{SiSiMe}_2\text{Br}$	0.73	0.52
$\text{IMe}_2\text{SiSiMe}_2\text{I}$	0.94	0.73
$\text{Me}_3\text{SiOBI}_2$	0.217	

^a $J_{\text{H}-19\text{F}} = 7.4$ Hz; ^b Reference 51; ^c Reference 136;

^d Reference 48; ^e Reference 69; ^f Reference 135.

Table VIII. ^1H N.M.R. Chemical Shifts for Boron Compounds

Compound	CDCl_3 (20%)		C_6H_6 (20%)
	Observed	Literature ^a	
MeBBr_2	1.43*	1.42	0.89
MeBI_2	1.67	1.66	1.27
Me_2BBr	1.14	1.14	
Me_2BI	1.33	1.34	

* The absence of two-bond coupling, $^{11}\text{B}-\text{C}-\text{H}$, in Me_2BX , MeBX_2 , is attributed to the high quadrupole moment of boron^{7,39}. Such coupling has been observed, however, in quaternary boron compounds such as $\text{Me}_3\text{N}\cdot\text{BX}_3$ ¹² and several other compounds^{6,16,96,141}.

^a Reference 109.

In an attempt to prove the presence of the above products, which could not be separated, it was necessary to convert them into derivatives that would verify their presence in the same mixture.

Table IX. Chemical shifts of adducts of trimethyl amine with boron compounds (δ in ppm, CDCl_3 used as solvent)

Adduct	δ (B-Me)	δ (N-Me)
$\text{Me}_3\text{N}\cdot\text{BBr}_3$	--	3.17 q
$\text{Me}_3\text{N}\cdot\text{BI}_3$	--	3.33 q
$\text{Me}_3\text{N}\cdot\text{BMeBr}_2$	0.87 b	3.0 b
$\text{Me}_3\text{N}\cdot\text{BMeI}_2$	1.37 b	3.1 b
$\text{Me}_3\text{N}\cdot\text{BMe}_2\text{I}$	0.61 b	2.82 b

b = broad, q = quartet

The addition of alcohol to the mixture of BI_3/TMS resulted in reaction of the products as follows:

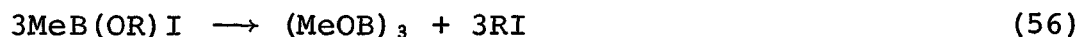
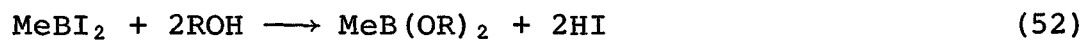


Table X. Chemical shifts of some derivatives arising from adding alcohol (ROH) to TMS/ BI_3 mixture (δ in ppm, CDCl_3 used as solvent)

R	δ RI	δ <u>Me</u> B(OR) ₂	δ <u>Me</u> ₂ BOR	δ <u>Me</u> BOR	δ Me ₃ SiOSiMe ₃
CH ₃	2.15	0.15	0.22	3.48	0.07
CH ₃ CH ₂	1.8, 2.17	0.12	0.19	1.2, 3.74	0.07
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C} \\ \\ \text{CH}_3 \end{array}$	1.94	0.19	0.37	1.94	0.07
ϕ -CH ₂	7.0, 4.09	0.24	0.34	7.0, 4.52	0.07

These N.M.R. data agreed favourably with the reported values^{48, 51, 109, 136}.

2. Combined Gas Chromatograph and Mass Spectrometry

The above derivatives were also identified by GC/MS. Mass Spectra by relative abundance of the derivatives arising from adding benzyl alcohol to TMS/ BI_3 mixture are given below as an example. All peaks of relative abundance below 2% are neglected unless they are important to fragmentation pathways.

Table XI. Tabular data for $\phi\text{CH}_2\text{I}$, $\phi\text{CH}_2\text{OSiMe}_3$, $\text{Me}_3\text{SiOSiMe}_3$ and $(\text{MeOB})_3$

1. $\phi\text{CH}_2\text{I}$					
m/e	Ion ⁺	Relative Abundance	m/e	Ion ⁺	Relative Abundance
218	$\text{C}_7\text{H}_7\text{I}$	0.4	90		7.0
128	HI	5.0	89		12.0
127	I	36.0	78		1.1
92		9.0	77	C_6H_5	1.0
91	C_7H_7	100.0			

2. $\phi\text{CH}_2\text{OSiMe}_3$					
m/e	Ion ⁺	Relative Abundance	m/e	Ion ⁺	Relative Abundance
180	$\text{C}_{10}\text{H}_{16}\text{OSi}$	1.7	137		1.7
167		1.7	136		1.7
166		3.3	135	$\text{C}_7\text{H}_7\text{OSi}$	15.0
165	$\text{C}_9\text{H}_{13}\text{OSi}$	26.7	108		6.7
150	$\text{C}_8\text{H}_{10}\text{OSi}$	1.7	107	$\text{C}_7\text{H}_7\text{O}$	6.7
149		4.2	105		6.7

continued

Table XI.

2. continued

m/e	Ion ⁺	Relative Abundance	m/e	Ion ⁺	Relative Abundance
92		9.2	78		15.0
91	C ₇ H ₇	100.0	77	C ₆ H ₅	30.0
90		2.5	76		3.3
89		6.7	75		8.3
79		31.7	74		5.0
			73	Me ₃ Si	11.7

3. Me₃SiOSiMe₃

m/e	Ion ⁺	Relative Abundance	m/e	Ion ⁺	Relative Abundance
162		0.00	106		0.2
151		0.3	105		1.0
150		0.9	104		0.2
149		7.0	103		1.2
148		14.7	102		0.5
147	Me ₅ Si ₂ O	100.0	101		0.7
134		0.2	89		0.2
133		1.7	88	Me ₃ SiO	0.2
132		0.9	87		1.0
131		5.3	75		1.7
119		0.4	74		1.7
118		0.2	73	Me ₃ Si	19.1
117		1.2	72		1.0
116		0.4	71		0.7
115		0.7		continued	

Table XI.

3. continued

m/e	Ion ⁺	Relative Abundance	m/e	Ion ⁺	Relative Abundance
67		1.2	59		6.2
66		13.0	58		0.8
61		0.5	57		0.5
60		0.6			

4. (MeOB)₃

m/e	Ion ⁺	Relative Abundance	m/e	Ion ⁺	Relative Abundance
128		0.7	94		0.1
127		0.7	93		0.2
126	(MeOB) ₃	7.3	71		0.1
125		5.1	70		0.3
124		1.6	69	MeO ₂ B ₂	9.5
123		0.4	68		5.1
113		0.5	67		1.3
112		2.4	66		0.2
111	Me ₂ O ₃ B ₃	100.0	57		0.1
110		71.0	56		0.2
109		14.5	55		2.0
108		2.0	54		0.8
97		0.5	53		0.5
96		0.6	52		0.2
95		0.3			

SUMMARY

1. Reactions of boron tribromide or boron triiodide with organic halides show that halogen exchange occurs at the carbon-halogen bond.
2. The rates of the reaction vary with the substituents on the carbon bearing the halogen in the organic halide. Further kinetic work along this line is indicated.
3. It appears that presence of a double bond in the organic halide reduces the chance of exchange reaction; true also in the case of halogens on an aromatic ring. Evidence for this is suggestive rather than conclusive. Further work could be done to prove this.
4. Organo-silicon compounds with any electronegative heteroatoms undergo carbon-silicon cleavage with boron triiodide or boron tribromide.
5. The presence of atoms such as oxygen or halogen bonded to silicon enhances silicon-oxygen or silicon-halogen bond cleavage.

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