decomposed at temperatures over 350°; nmr in D_2O (ppm upfield from exchanging H_2O signal): 2.53 (d, J = 14 Hz, PCH_3), 2.31 (s), and 1.93–2.83 (m).

Anal. Calcd for $C_6H_{14}BrP$: C, 36.57; H, 7.16. Found: C, 36.97; H, 7.35.

Dimethyl-*n*-butylphosphine Oxide (23). *n*-Butyldichlorophosphine, bp 92–99° (79 mm) (lit.[32] 58–60° (22 mm)), prepared by a literature method,[32] was made to react with methylmagnesium bromide[33] to yield dimethyl-*n*-butylphosphine, bp 56–60° (72 mm) (lit.[33] 69–70° (100 mm)). The latter phosphine (29.7 g) was dissolved in 250 ml of CH_2Cl_2 and 32.5 g of *t*-butyl hydroperoxide was added with vigorous stirring to the solution at −20°. After concentration, the residue was distilled to give **23**, a low melting, hygroscopic solid, in 95% yield, bp 70–73° (0.25 mm); nmr (CH_2Cl_2) δ 1.05 (d, J = 14.5 Hz CCH_3), 1.38 (d, J = 12.5 Hz, $P(O)CH_3$), and 0.72–1.89 (m, CH_2); δ ^{31}P nmr = −38.3 ppm.

Anal. Calcd for $C_6H_{15}OP\cdot0.5H_2O$: C, 50.32; H, 11.26. Found: C, 50.50; H, 11.36.

Reaction of 22a with Sodium Hydroxide. To 5.91 g of **22a** was added 30 ml of 2 M NaOH and the mixture refluxed until no further change in gas volume was evident (about 4 days). Benzene was added, the water removed by azeotropic distillation, the solution concentrated, and the residue distilled and collected as one fraction. This was examined by ^{31}P nmr and the phosphorus signals shown to be identical with those of authentic **22b** and **23**. Integration of the signals gave a ratio of **22b**/**23** of 3.5:1. A second run was performed under identical conditions, and an aliquot was titrated with standard acid showing the reaction to have proceeded 99 ± 1% to completion.

Acknowledgments. The author wishes to express his indebtedness to Drs. D. B. Denney and D. Z. Denney for their helpfulness and to the School of Chemistry, Rutgers, The State University, New Brunswick, N. J., for generous use of facilities.

---

(32) R. B. Fox, *J. Amer. Chem. Soc.*, **72**, 4147 (1950).

(33) G. Kamai and L. A. Khismatullina, *Zh. Obshch. Khim.*, **26**, 3426 (1956); *Chem. Abstr.*, **51**, 9512 (1957).

Stereochemistry of Asymmetric Silicon. XII. Reactions of Silicon–Oxygen and Silicon–Nitrogen Compounds with Boron Halides[1,2]

Leo H. Sommer,[3] Joel D. Citron, and George A. Parker

Contribution from the Departments of Chemistry, University of California, Davis, California, and The Pennsylvania State University, University Park, Pennsylvania.

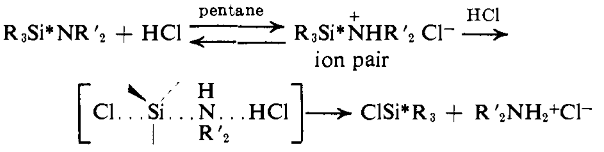
Received February 1, 1969

Abstract: The stereochemistry of the reactions of a variety of optically active alkoxysilanes and aminosilanes with boron halides has been studied. For these reactions, which yield the halosilane, the simplest and most obvious mechanistic possibility would be a four-center mechanism and this has been previously proposed by other authors. We have found that most of the reactions proceed with *inversion* of configuration. (The major exception is BCl_3 plus R_3Si^*OR'.) Thus, clearly, the general mechanistic situation is not the one previously assumed and the present paper discusses new mechanistic possibilities for these interesting reactions of asymmetric silicon with strong Lewis acids.

Although the dynamic stereochemistry of reactions of silicon–oxygen[4] and silicon–nitrogen bonds[5] with a wide variety of reagents is known, a systematic study of the factors affecting stereochemical path with strong aprotic acids as reagents has not yet been reported.

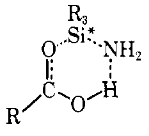
The boron halides are strong Lewis acids and, in contrast to HX, BX_3 would not be expected to very rapidly yield halide ion subsequent to coordination with a nitrogen or oxygen function. Thus, the boron halides posed an extremely interesting mechanistic question concerning whether, after coordination, the lesser ionic character of the boron–halogen bond relative to the hydrogen–halide bond would lead to retention of configuration *via* a four-center SNi–Si transition state. This question arises because the reaction of aminosilanes with hydrogen halides such as HCl usually proceeds with inversion of configuration whereas an acid of decreased strength such as benzoic changes the stereochemistry to predominant *retention of* configuration[5] with $R_3Si^*NH_2$.

For the inversion reactions of aminosilanes with HCl our preferred mechanism was formulated as in (1).



$$R_3Si^*NR'_2 + HCl \underset{}{\overset{\text{pentane}}{\rightleftharpoons}} \underset{\text{ion pair}}{R_3Si^*\overset{+}{N}HR'_2\,Cl^-} \xrightarrow{HCl} \left[Cl\cdots Si\cdots \underset{R'_2}{\overset{H}{N}}\cdots HCl\right] \longrightarrow ClSi^*R_3 + R'_2NH_2^+Cl^- \quad (1)$$

In the reaction of $R_3Si^*NH_2$ with benzoic acid compared to HCl, the combination of lowered acidity of the reagent and low steric requirements of the $-NH_2$ group changed the predominant stereochemistry from 91% inversion of configuration with HCl to 79% retention with benzoic acid and the transition state for this latter retention reaction was formulated according to I. Evidence



I

---

[1] For the preceding paper in this series, see: L. H. Sommer and J. McLick, *J. Am. Chem. Soc.*, **91** 2001 (1969).

[2] We are grateful for generous support of this work by Dow Corning Corporation.

[3] Address inquiries to this author at the Department of Chemistry, University of California, Davis, California.

[4] For the most recent paper in this series dealing with this subject and for references to earlier papers, see: L. H. Sommer and H. Fijimoto, *J. Am. Chem. Soc.*, **90**, 982 (1968).

[5] L. H. Sommer and J. D. Citron, *ibid.*, **89**, 5797 (1967).

Table I. Stereochemistry of Cleavages of Silicon–Oxygen Bonds by Boron Halides

Substrate[a]	Solvent	Boron halide	Product[a]	Predominant stereochemistry,[c] %
(+)-R_3Si^*OMe	Pentane	BCl_3	(−)-R_3Si^*Cl	Retention, 92
(+)-R_3Si^*OMe	Pentane	BF_3	(−)-R_3Si^*F	Inversion, 89
(+)-R_3Si^*OMe	Pentane	$BF_3 \cdot OEt_2$	(−)-R_3Si^*F	Inversion, 68
(+)-R_3Si^*OMe	Et_2O	$BF_3 \cdot OEt_2$	(−)-R_3Si^*F	Inversion, 73
(+)-R_3Si^*OH	Benzene	$BF_3 . OEt_2$	(−)-R_3Si^*F	Inversion, 76
(+)-R_3Si^*OK	Xylene	$BF_3 \cdot OEt_2$[d]	(+)-R_3Si^*F	Inversion, 75
(+)-$R_3Si^*OSi^*R_3$	Xylene	$BF_3 \cdot OEt_2$	No reaction	
(+)-R_3Si^*O-(−)-Men[b]	Et_2O	$BF_3 \cdot OEt_2$	(+)-R_3Si^*F	Inversion, 89
(+)-R_3Si^*O-*t*-Bu	Et_2O	$BF_3 \cdot OEt_2$	(+)-R_3Si^*F	Inversion, 70
(+)-$R_3'Si^*OMe$	Pentane	BCl_3	(+)-$R_3'Si^*Cl$	Retention, 100
(+)-$R_3'Si^*OMe$	Pentane	BF_3	(−)-$R_3'Si^*F$	Inversion, 100
(+)-$R_3'Si^*OMe$	Pentane	$BF_3 \cdot OEt_2$	(−)-$R_3'Si^*F$	Inversion, 84
(+)-$R_3''Si^*OMe$	Pentane	BCl_3	(+)-$R_3''Si^*Cl$	Retention, 92
(+)-$R_3''Si^*OMe$	Pentane	BF_3	(−)-$R_3''Si^*F$	Inversion, 97
(+)-$R_3''Si^*OMe$	Pentane	$BF_3 \cdot OEt_2$	(−)-$R_3''Si^*F$	Inversion, 85

[a] R_3Si^* is α-naphthylphenylmethylsilyl, $R_3'Si^*$ is neopentylphenylmethylsilyl, and $R_3''Si^*$ is benzhydrylphenylmethylsilyl. For simplicity, all starting materials are the *d* isomer. [b] See ref 8a; -O-Men is menthoxy. [c] 90% inversion means that the product was 90% inverted and 10% retained (equivalent to 80% optical purity) if optically pure starting material was used. [d] Excess.

Table II. Stereochemistry of Reactions of Silylamines with Boron Halides

Silylamine[a,b]	Boron halide	Solvent	Product	Predominant stereochemistry,[d] %
(+)-R_3Si^*Pyr	BF_3	Pentane	(+)-R_3Si^*F	Retention, 54
(+)-R_3Si^*Pyr	$BF_3 \cdot OEt_2$	Et_2O	(−)-R_3Si^*F	Inversion, 57
(+)-R_3Si^*NHBu	BF_3	Pentane	(−)-R_3Si^*F	Inversion, 62
(+)-R_3Si^*NHBu	$BF_3 \cdot OEt_2$	Et_2O	(−)-R_3Si^*F	Inversion, 74
(+)-$R_3Si^*NH_2$	BF_3	Pentane	(+)-R_3Si^*F	Inversion, 81
(+)-R_3Si^*Pyr	BCl_3	Pentane	(+)-R_3Si^*H[c]	Inversion, 68
(+)-R_3Si^*NHBu	BCl_3	Pentane	(+)-R_3Si^*H[c]	Inversion, 90
(+)-$R_3Si^*NH_2$	BCl_3	Pentane	(−)-R_3Si^*H[c]	Inversion, 92
(+)-R_3Si^*Pyr	BBr_3	Pentane	(+)-R_3SiH[c]	Inversion, 81
(+)-R_3Si^*NHBu	BBr_3	Pentane	(+)-R_3Si^*H[c]	Inversion, 73

[a] For relative configurations of the silylamines, see ref 5. [b] R_3Si^* is naphthylphenylmethylsilyl, Pyr is 1-pyrrolidinyl, and NHBu is isobutylamino. [c] The initial product was reduced with $LiAlH_4$. Predominant stereochemistry values for the boron halide reaction assume 100% inversion for the reduction.[8a] [d] See footnote *c* in Table I.

for I derives from a change to predominant inversion of configuration when the steric requirements of the reagent were greatly increased through use of mesitoic acid.[5] Molecular models indicated substantial hindrance to formation of I in this case.

Results

The reactions of boron halides with silicon–oxygen bonds to give halosilanes are well known.[6,7] In Table I are reported the results of our present stereochemical studies which dealt with cases for which the relative configurations of reactants and products were known from previous work.[8] Thus, the predominant stereochemical path was readily deduced.

Since the SNi-Si mechanism and *retention* of configuration are of great importance in organosilicon stereochemistry as indicated, for example, by recent studies revealing stereochemistry crossover (from predominant inversion to retention of configuration and *vice versa*) with relatively small variation in the reagent and solvent,[4] we have previously reported stereospecificity for organosilicon reactions on the assumption of a mixture of inversion and retention stereochemistry—in contrast to organic stereochemistry, in which racemization and inversion are usually the two main paths and stereospecificity equates with optical purity. To avoid dichotomy of usage of the term *stereospecificity* and to maintain what we feel to be a realistic method of mechanistic appraisal for organosilicon stereoreactions in which racemization is probably a minor path, we have used the term *predominant stereochemistry* in Tables I and II in this paper and calculated the extent (%) to which the reaction follows the major stereochemical path on the assumption of a mixture of inversion and retention stereochemistry

$$\text{predominant stereochemistry, } \% = 100 \times \frac{\text{major stereochemical product}}{\text{total product}}$$

Several points in Table I are noteworthy. Reactions with boron trifluoride or its etherate invariably give *inversion* of configuration at silicon. In contrast, boron trichloride and the methoxysilanes of three different optically active systems give excellent *retention* of configuration.

The reactions of boron halides with silicon–nitrogen bonds are well known and give the halosilanes, in many cases *via* demonstrable formation of the aminosilane–boron halide complex at low temperature.[9] Table II

---

(6) C. Eaborn, "Organosilicon Compounds," Academic Press, New York, N. Y., 1960, pp 170–173.

(7) V. Bazant, V. Chvalovsky, and J. Rathousky, "Organosilicon Compounds," Academic Press, New York, N. Y., 1965, pp 50, 60, and 88.

(8) (a) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964); (b) L. H. Sommer, C. L. Frye, and G. A. Parker, *ibid.*, **86**, 3276 (1964); (c) L. H. Sommer, K. W. Michael, and W. D. Korte, *ibid.*, **89**, 868 (1967).

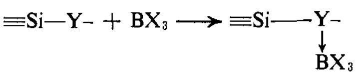
reports the results of our stereochemical studies. Assignment of predominant stereochemical path is based upon relative configurations of reactants and products established by previous work.[5]

With the exception of the first reaction in Table II, which proceeds with slight preference for retention, the reactions in both tables using boron trifluoride or its etherate proceed with predominant *inversion* of configuration. The dramatic difference between the oxygen and nitrogen compounds lies in their stereochemical behavior with boron trichloride. The former give excellent *retention* and the latter excellent *inversion* of configuration with BCl_3.

At this point, two very general mechanistic comments can be made. (a) The reactions of boron trifluoride or its etherate with either silicon–oxygen or silicon–nitrogen bonds do not usually involve a dominant, simple SNi–Si four-center mechanism. (b) The dynamic stereochemistry found with boron trichloride is more sensitive to reactant structure than is that found for the fluoride. The next section comprises a more detailed mechanism discussion.

Discussion of Mechanism

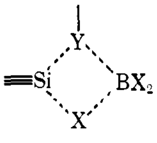
The reactions which are included in Tables I and II generally proceed as rapidly as the Lewis acid is added. Furthermore, for other displacement reactions at silicon in which the nature of the reagent does not permit coordination with oxygen or nitrogen, reaction is slow. This usually occurs in base-catalyzed reactions in which the leaving group (formally), an oxide or amide, is poor.[10] These facts, taken together with the low-temperature isolation of coordination complexes of boron halides with silicon–nitrogen and silicon–oxygen compounds,[9,11] strongly suggest that the first step in the boron trihalide reactions involves the conversion of the poor (highly basic) leaving groups in Tables I and II, to better leaving groups by coordination with BX_3. Schematically, this can be formulated according to (2).



$$\equiv\text{Si—Y-} + BX_3 \longrightarrow \equiv\text{Si—}\underset{\displaystyle BX_3}{\underset{\downarrow}{\text{Y-}}} \qquad (2)$$

$Y = N, O;\ X = F, Cl, Br$

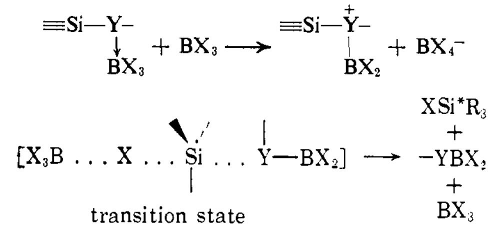
Several authors have postulated that (2) is followed by operation of a four-center process for BX_3 reactions of both silicon–oxygen[11,12] and silicon–nitrogen bonds.[13,14]



II

However, transition state II would lead to formation of the silicon halide with *retention* of configuration and only 4 out of 25 reactions in Tables I and II give this stereochemistry. Clearly, the other 21 reactions must pursue a different path.

In order to give *inversion* of configuration, a halide ion (which is probably complexed in the nonpolar media used) likely is involved in SN2–Si attack[15] at the rear of the silicon and displaces the oxygen or nitrogen whose leaving group ability has been enhanced by coordination. There are several possible alternative steps subsequent to (2), involving different leaving groups and different attacking nucleophiles which can furnish halide ion for SN2–Si attack. In our view, one of the most probable of these sequences approximates mechanism 3 given below. The first step of (3) improves



$$\equiv\text{Si—}\underset{\displaystyle BX_3}{\underset{\downarrow}{\text{Y-}}} + BX_3 \longrightarrow \equiv\text{Si—}\underset{\displaystyle BX_2}{\underset{|}{\overset{+}{\text{Y}}}}\text{-} + BX_4^-$$

$$[X_3B\ldots X\ldots Si\ldots Y—BX_2] \longrightarrow XSi^*R_3 + {-YBX_2} + BX_3 \qquad (3)$$

the leaving group which acquires a formal positive charge. In the same step the halide ion needed for nucleophilic attack on silicon becomes part of a BX_4^- species. The latter is preferable to X^- as the nucleophile because the negative charge is now dispersed over a larger ion, which should lower its energy in a nonpolar medium, and this dispersal of charge should then assist in the transport of the nucleophile to the rear of the silicon center. Furthermore, the unassisted removal of X^- from $\equiv SiYBX_3$ and its transport in a nonpolar medium seem unlikely, as does also simple rearward attack of a second BX_3 molecule on $\equiv SiYBX_3$ providing a nucleophilic halide ion for SN2–Si displacement.

Concerning the variation in stereochemical path observed for the BCl_3 reagent with change in reactant, it is interesting to note that ~20% *inversion* stereospecificity (~20% optical purity in the product) was found for the reaction of (+)-ethyl 1-methylheptyl ether with BCl_3 to give (−)-2-chlorooctane,[16] and that ~50% *retention* stereospecificity was found for the reaction of 3 mol of (+)-α-phenylethyl chloride.[16] For the latter reaction the stereospecificity found is a minimum figure, since a separate experiment showed that the chloride is racemized by BCl_3 at a substantial rate.[16] Such is not the case for the 2-chlorooctane.

As supporting evidence for the occurrence of the first step of (3) in the inversion reactions, it might be noted that rapid decomposition of $(RO)_2BCl$ and $ROBCl_2$ by ~1% Lewis acid (A) was noted long ago and proposed to involve the following process as a first step.[17]

$$ROBCl_2 + A \rightleftarrows [ROBCl]^+ + [ACl]^-$$

In the above general formulation, A can be $FeCl_3$, BCl_3, or $AlCl_3$, and a subsequent step produced 2-chlorooctane with ~50% *inversion* stereospecificity when A was BCl_3.[17] In our judgment, it seems very likely that the inversion reactions in Tables I and II have a mechanism which involves (2) and (3) and that some of the

---

[9] For a recent review, see: O. J. Scherer, *Organometal. Chem. Rev.*, **3**, 281 (1968).

[10] L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, pp 56–58.

[11] H. J. Emeleus and M. Onyszchuk, *J. Chem. Soc.*, 604 (1958); M. Onyszchuk, *Can. J. Chem.*, **39**, 808 (1961).

[12] E. Wiberg and U. Kruerke, *Z. Naturforsch.*, **8b**, 608, 609 (1953).

[13] M. Becke-Goehring and H. Krill, *Chem. Ber.*, **94**, 1059 (1961).

[14] U. Wannagat, *Advan. Inorg. Chem. Radiochem.*, **6**, 225 (1964).

[15] L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *J. Am. Chem. Soc.*, **89**, 857 (1967).

[16] W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 1020 (1951).

[17] W. Gerrard and M. F. Lappert, *ibid.*, 3084 (1955).

inversion reactions found by Gerrard and Lappert during their studies of BCl_3 with R*OR and R*OH[16,17] also proceed *via* the same general mechanism.[18]

Concerning the *retention* reactions of BCl_3 in Table I, it seems clear that a mechanism approximating transition state II obtains, but the interesting questions concern the reasons for: (a) stereochemistry crossover within Table I on changing from boron trifluoride to the trichloride; (b) stereochemistry crossover engendered with BCl_3 on changing from a silicon–oxygen reactant in Table I to a silicon–nitrogen reactant in Table II. Concerning a, it is likely that an important contributing factor is provided by the greater Lewis acid strength of BCl_3 *vs.* BF_3.[19] This factor would provide greater weakening of the silicon–oxygen bond and make the silicon center more effective for accepting a chloride ion intramolecularly in the complex formed in (2). With regard to b, it is probable that, relative to oxygen, the greater ability of nitrogen to stabilize a positive charge results in insufficient weakening of the silicon–nitrogen bond to permit intramolecular four-center attack of a chloride ion in an SNi–Si retention mechanism. These explanations for a and b are clearly in accord with the predominant retention stereochemistry found for the α-phenylethyl–oxygen cleavages with BCl_3. Because of the enhanced ability of the α-phenylethyl system to delocalize positive charge, relative to the 2-octyl system, the carbon–oxygen bond in the former is relatively easily weakened by coordination with a BCl_3 molecule and a four-center mechanism is thereby favored. In this carbon case, a carbonium ion pair may be involved as an intermediate. In the silicon cases, a simple SNi–Si mechanism is probably involved in the retention reactions in Table I.

Perhaps the most important general feature of the above stereochemical results lies in the finding of *inversion of configuration* as the most common path for boron halide reactions with silicon–oxygen and silicon–nitrogen bonds despite the fact that it might reasonably have been predicted that such chemical situations would be ideal for operation of SNi–Si four-center mechanisms. Thus, the actual results emphasize again the importance of the SN2–Si mechanism and the Walden inversion.

Experimental Section

All optically active starting materials were prepared by known procedures, and products were identified by comparison of their infrared spectra with those of authentic samples. Boron trichloride and boron trifluoride were obtained as gases from the Matheson Co., Inc., and used as received. Boron tribromide (Trona Chemical Co.) was used without further purification. Boron trifluoride etherate was distilled before use, bp 120–125°. Solvents were dried by standard methods.

Reaction of Boron Trifluoride with Silylamines. A filter flask containing a solution of 1.49 g of (−)-N-isobutyl-α-naphthylphenylmethylsilylamine, $[\alpha]_D$ −4.9° (*c* 2.4, pentane), in 35 ml of pentane was flushed with nitrogen, and then boron trifluoride was bubbled in for 1 min. A white solid precipitated immediately. After again sweeping with nitrogen, the mixture was washed several times with water, and then dried over sodium sulfate. A rotation on the crude material gave $[\alpha]_D$ +10.4° (*c* 1.7, pentane), but an infrared spectrum indicated the presence of silanol and other compounds in addition to α-naphthylphenylmethylfluorosilane. The product was placed on an 18 × 0.5 in. silica gel column and eluted with benzene–pentane (25:75, v/v) solvent. The product (+)-α-naphthylphenylmethylfluorosilane, $[\alpha]_D$ +9.7° (*c* 0.7, pentane), was obtained in 16% (0.18 g) yield. By a similar procedure, (−)-α-naphthylphenylmethyl(1-pyrrolidinyl)silane (2.4 g), $[\alpha]_D$ −20.3° (*c* 1.0, pentane), was treated with BF_3, giving 0.14 g (16%) of (−)-naphthylphenylmethylfluorosilane, $[\alpha]_D$ −3.3° (*c* 1.0, pentane).

(−)-α-Naphthylphenylmethylsilylamine [0.62 g, $[\alpha]_D$ −4.5° (*c* 0.9, pentane)] was reacted in a like manner to yield 0.13 g (21%) of (−)-α-naphthylphenylmethylfluorosilane, $[\alpha]_D$ −29.1° (*c* 0.3, pentane).

Reaction of Silylamines with Boron Trifluoride Etherate. In a 250-ml filter flask the solvent was stripped from a solution of 2.4 g of (−)-α-naphthylphenylmethyl(1-pyrrolidinyl)silane, $[\alpha]_D$ −20.3° (*c* 1.0, pentane), in 174 ml of pentane until the total volume was approximately 10 ml. Ether (150 ml) was added, and then boron trifluoride was bubbled through. The solvent was removed under vacuum until about 15 ml remained, at which time the solution was diluted with 150 ml of pentane. The mixture was washed with water and dried over sodium sulfate. After filtration, the solution was divided into two equal portions.

One part was stripped of solvent, and the yellow residue remaining was shown to be about 80% α-naphthylphenylmethylfluorosilane by infrared analysis. This was dissolved in pentane, poured onto a silica gel column, and eluted with a benzene–pentane (30:70, v/v) solvent. This yielded 0.44 g (45%) of (+)-α-naphthylphenylmethylfluorosilane, $[\alpha]_D$ +5.8° (*c* 1.8, pentane). The other half of the solution was freed of solvent and gave 0.87 g (90%) of crude product.

By a similar procedure, 0.30 g (24%) of (+)-α-naphthylphenylmethylfluorosilane, $[\alpha]_D$ +20.7° (*c* 1.2, pentane), was obtained from the reaction of 1.5 g of (−)-N-isobutyl-α-naphthylphenylmethylsilylamine, $[\alpha]_D$ −4.9° (*c* 4.8, pentane).

Reactions of Silylamines with Boron Trichloride. To 2.1 g of (+)-N-isobutyl-α-naphthylphenylmethylsilylamine (prepared from (+)-α-naphthylphenylmethylchlorosilane, $[\alpha]_D$ +5.1°)[5] dissolved in 175 ml of pentane in a 250-ml filter flask flushed with helium was added boron trichloride gas for 4 min. A precipitate formed immediately. After addition was complete, a small sample was removed for infrared analysis. The infrared spectrum of this sample indicated the presence of boron compounds and some disiloxane, but it was mostly chlorosilane.

The remainder of the material was added to a solution of 4 g of lithium aluminum hydride in 150 ml of ether. After 15 min, the hydride was decomposed with acetone, the resulting mixture washed with cold dilute hydrochloric acid and water (four times), dried over sodium sulfate, and filtered, and the solvent stripped. The crude product weighed 1.53 g and had a specific rotation of +10.8°. The material was dissolved in pentane and placed on a 24 × 0.5 in. silica gel column. After elution with benzene–pentane solvent (30:70, v/v), 0.77 g (55%) of (+)-α-naphthylphenylmethylsilane was obtained, $[\alpha]_D$ +22.1° (*c* 3.1, pentane). By a similar procedure, boron trichloride was treated with 1.87 g of (+)-α-naphthylphenylmethyl (1-pyrrolidinyl)silane, $[\alpha]_D$ +17.9° (*c* 1.7, pentane), to give 0.69 g (53%) of (+)-α-naphthylphenylmethylsilane, $[\alpha]_D$ +9.7° (*c* 2.8, pentane).

By a similar procedure, 0.40 g of (−)-α-naphthylphenylmethylsilylamine, $[\alpha]_D$ −4.5° (*c* 1.2, pentane), gave, after reaction with BCl_3 and $LiAlH_4$, 0.10 g (27%) of (+)-α-naphthylphenylmethylsilane, $[\alpha]_D$ +27.5°.

Reactions of Silylamines with Boron Tribromide. To a solution of 2.1 g of (+)-N-isobutyl-α-naphthylphenylmethylsilylamine, $[\alpha]_D$ +3.9° (*c* 4.3, pentane), in 195 ml of pentane was added two 1-ml portions of boron tribromide, and a granular white precipitate formed at once. The mixture was then added to 4 g of lithium aluminum hydride dissolved in 150 ml of ether, giving a vigorous exothermic reaction that boiled the solvent. After standing 20 min at room temperature the hydride was decomposed with acetone, and then the organic layer was washed with cold dilute hydrochloric acid and water, and then dried over sodium sulfate. After removal of solvent, the residue was chromatographed on an 18 × 0.5 in. silica gel column, using benzene–pentane (30:70) as the eluent. This gave 1.05 g (62%) of pure (+)-α-naphthylphenylmethylsilane, $[\alpha]_D$ +12.1° (*c* 4.2, pentane).

By a similar procedure (+)-α-naphthylphenylmethyl(1-pyrrolidinyl)silane (2.3 g), $[\alpha]_D$ +18.7° (*c* 1.3, pentane), gave, after re-

---

[18] In their papers, Gerrard and Lappert[16,17] tend to regard all of these reactions as proceeding *via* carbonium ion intermediates. We believe it is unlikely that this is true for all their reactions but may be true for some—particularly for those in which intramolecular rearrangement of the R group occurred.

[19] H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, 78, 2137 (1956); W. Dutton, W. G. Paterson, and M. Onyszchuk, *Proc. Chem. Soc.*, 149 (1960).

action with BBr_3 and $LiAlH_4$, 0.64 g (36%) of (+)-α-naphthylphenylmethylsilane $[\alpha]_D$ +15.3° (*c* 2.6, pentane).

Reactions of Methoxysilanes with Boron Trifluoride. Into a 250-ml suction flask, fitted with a porous glass gas inlet tube and connected to a Gilman trap from the side arm, were placed (−)-α-naphthylphenylmethylmethoxysilane [1.05 g, $[\alpha]_D$ −17.5° (*c* 2.7, pentane)] and 100 ml of pentane. The solution was cooled to 0° in an ice bath, and boron trifluoride was bubbled into the solution. A white precipitate formed as the boron trifluoride was added, but after about 2 min, the material dissolved to give a clear solution. The boron trifluoride was added for several more minutes to ensure complete reaction. Most of the solvent and excess boron trifluoride as well as volatile products were removed on the steam bath; the last traces were removed at reduced pressure to give (+)-α-naphthylphenylmethylfluorosilane (0.97 g, 95% yield), $[\alpha]_D$ +35° (*c* 9.2 in pentane), as a colorless syrup which crystallized on cooling.

In a similar manner, 0.50 g of (−)-phenylneopentylmethylmethoxysilane, $[\alpha]_D$ −6.48° (*c* 10.0, pentane), was treated with BF_3 to give 0.44 g (93%) of (+)-phenylneopentylmethylfluorosilane, $[\alpha]_D$ +2.5° (*c* 4.4, pentane).[20]

By a similar procedure, (−)-benzhydrylphenylmethylmethoxysilane (1.18 g), $[\alpha]_D$ −21.2° (*c* 9.7, pentane), gave 0.85 g (76%) of (+)-benzhydrylphenylmethylfluorosilane, $[\alpha]_D$ +7.8° (*c* 5.2, pentane).[21]

Reactions of Methoxysilanes with Boron Trifluoride Etherate. (+)-α-Naphthylphenylmethylmethoxysilane (0.27 g), $[\alpha]_D$ +11° (*c* 2.1, pentane), was dissolved in 10 ml of pentane in a 2.5-dm polarimeter tube. The solution had α_{obsd} +0.66°. Then boron trifluoride etherate (0.40 ml) was added from a syringe to the polarimeter tube. The reactants were mixed well and the rotation was read as soon as possible (*ca.* 30 sec). The observed rotation had decreased to zero or a slightly negative value. After 2 hr at room temperature the rotation was α_{obsd} −0.50°. This value did not change after 24 hr. The solution was then transferred quantitatively to a 250-ml suction flask and the pentane and excess boron trifluoride etherate were removed at reduced pressure. Syrupy (−)-α-naphthylphenylmethylfluorosilane (0.18 g, 69%), $[\alpha]_D$ −10.4° (*c* 1.3, pentane), was obtained.

By a similar procedure, except that the solvent was diethyl ether, 0.32 g of (+)-α-naphthylphenylmethylmethoxysilane, $[\alpha]_D$ +8.4° (*c* 1.8, ether), gave, after reaction with boron trifluoride etherate, 0.22 g (69%) of (−)-α-naphthylphenylmethylfluorosilane, $[\alpha]_D$ −9.9° (*c* 1.3, pentane). There was a small amount (by infrared spectrum) of disiloxane in the product.

In a like manner, (−)-phenylneopentylmethylmethoxysilane (2.03 g), $[\alpha]_D$ −8.13° (*c* 13.5, pentane), was treated with boron trifluoride etherate to afford (+)-phenylneopentylmethylfluorosilane (1.42 g, 74%), $[\alpha]_D$ +2.0° (*c* 4.2, pentane).[20]

By a similar procedure, 3.00 g of (−)-benzhydrylphenylmethylmethoxysilane, $[\alpha]_D$ −17.0° (*c* 12.8, pentane), was treated with boron trifluoride etherate to yield 0.98 g (34%) of (+)-benzhydrylphenyl methylfluorosilane, $[\alpha]_D$ +5.1° (*c* 4.1, pentane).[21]

Reactions of Methoxysilanes with Boron Trichloride. Into a 250-ml suction flask, fitted with a dropping funnel, and connected from the side arm to a Gilman sulfuric acid trap, were placed (−)-α-naphthylphenylmethylmethoxysilane [0.80 g, $[\alpha]_D$ −17.5° (*c* 2.7 in pentane)] and 100 ml of pentane. The flask and contents were cooled to 0° by immersion in an ice bath. A solution of boron trichloride (*ca.* 4 ml) in 50 ml of pentane was placed in the dropping funnel, which was then connected to a Gilman trap. The boron trichloride solution was added rapidly to the methoxysilane solution. As the reagents were mixed, a white solid formed in the flask; at the end of the addition, however, the solid had disappeared. Most of the solvent was removed by gentle heating on the steam bath until about 25 ml of solution remained. The last few milliliters of pentane were removed at reduced pressure with no heating. A syrup was obtained which was not completely pentane soluble. Filtration and solvent removal yielded (+)-α-naphthylphenylmethylchlorosilane (0.51 g, 62% yield), $[\alpha]_D$ +5.1° (*c* 3.1, pentane).

By a similar procedure, 0.25 g of (−)-phenylneopentylmethylmethoxysilane, $[\alpha]_D$ −6.48° (*c* 10.0, pentane), afforded, after reaction with boron trichloride, 0.19 g (75%) of (−)-phenylneopentylmethylchlorosilane, $[\alpha]_D$ −4.0 (*c* 2.7, pentane).[20]

In a similar manner, (−)-benzhydrylphenylmethylmethoxysilane (2.84 g), $[\alpha]_D$ −16.1° (*c* 16.3, pentane), was treated with boron trichloride to yield (−)-benzhydrylphenylmethylchlorosilane (2.41 g, 84%), $[\alpha]_D$ −7.1° (*c* 18.6, pentane).[21]

Reaction of R_3Si^*-O-*t*-Bu with Boron Trifluoride Etherate.[22] A solution of 2.98 g of (−)-α-naphthylphenylmethyl-*t*-butoxysilane, $[\alpha]_D$ −25.9° (*c* 4.8, pentane), in 20 ml of ether was placed in a polarimeter tube (*l* 2.5 dm), and the observed rotation was −7.30°. Ten milliters of boron trifluoride etherate was added, and within 5 min the rotation had decreased to −2.06°. After 6 hr, the rotation remained constant at −2.75°. After 20-hr total time, the solution was diluted with 150 ml of pentane, and then washed with water, dried over anhydrous Na_2SO_4, and evacuated free of solvent, to yield a residue, which upon crystallization from pentane afforded 1.17 g (47%) of (−)-α-naphthylphenylmethylfluorosilane, $[\alpha]_D$ −18.5° (*c* 8.3, pentane).

Attempted Reaction of $(R_3Si^*)_2O$ with Boron Trifluoride Etherate. (−)-1,3-Di-α-naphthyl-1,3-diphenyl-1,3-dimethyldisiloxane (0.15 g) was dissolved in 10 ml of *p*-xylene in a 2.5-dm polarimeter tube, and the observed rotation was −0.62°. Then 0.10 ml of boron trifluoride etherate was added. There was no change in the rotation after 49 hr.

Reaction of R_3Si^*OH with Boron Trifluoride Etherate. (+)-α-Naphthylphenylmethylsilanol (0.52 g, 2.0 mmol), $[\alpha]_D$ +22° (*c* 4.9, benzene), was dissolved in 10 ml of benzene, and the solution was transferred to a 2.5-dm polarimeter tube. The observed rotation was +2.71°. Boron trifluoride etherate (0.26 ml, 2.0 mmol) was added from a hypodermic syringe to the (+)-silanol solution. The rotation was read as soon as possible after mixing and had changed to −0.63°. After 20 hr the rotation reached a constant value of −1.65°. To be certain the reaction was complete, 0.20 ml more boron trifluoride etherate was added; the rotation of the solution did not change. The benzene solution was transferred quantitatively to a separatory funnel, 80 ml of pentane was added, and the resulting solution was washed three times with cold water. The organic layer was dried over Drierite for 1 hr. Solvent removal with an aspirator gave (−)-α-naphthylphenylmethylfluorosilane (0.46 g, 87% yield), $[\alpha]_D$ −11.3° (*c* 2.7, pentane), as an oil. The infrared spectrum (CCl_4 solution) of the product showed a very strong Si–F absorption (11.6–11.8 μ) and a weak O–H maximum at 2.8 μ; the latter maximum is due to the presence of a small amount of silanol. The (−)-fluorosilane was formed with 76% net inversion of configuration.

Reaction of R_3Si^*OK with Boron Trifluoride Etherate. To a solution of 1.81 mmol of potassium α-naphthylphenylmethylsilanolate, $[\alpha]_D$ +65° (*c* 6.3, xylene), in 20 ml of xylene was added 2 ml (15.6 mmol) of boron trifluoride etherate. A small amount of material precipitated. After standing 7 hr the material was filtered, and the solvent was stripped under vacuum with heating. The slightly yellow syrup had $[\alpha]_D$ +99° (*c* 1.2, pentane). An infrared spectrum had strong absorption at 7.5 and 11.7 μ which probably indicated B–O and Si–F, respectively. The syrup was chromatographed over silica gel and eluted with benzene–pentane (12:88, v/v) solvent. From this, 0.13 g (27%) of (+)-α-naphthylphenylmethylfluorosilane was obtained, $[\alpha]_D$ +21° (*c* 1.0, pentane).

Observation of variation of the optical rotation during the course of a similar experiment showed that a levorotatory intermediate was rapidly formed from (+)-R_3Si^*OK and then slowly gave (+)-R_3Si^*F as the end product. Rotation passed through zero after about 30 hr, and took 11 days to reach a maximum positive value.

When equimolar amounts of $BF_3 \cdot Et_2O$ and (+)-R_3Si^*OK in xylene were used, in contrast to the above study a levorotatory product, presumably mainly (−)-$R_3Si^*OBF_2$, was formed and the rotation remained constant and negative for 28 hr. Attempts to isolate pure (−)-$R_3Si^*OBF_2$ were unsuccessful due to some contamination with other substances.

---

(20) This study was performed by K. W. Michael.

(21) This study was performed by W. D. Korte.

(22) This study was performed by C. L. Frye.