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Electronic Effects and the Stereochemistries in Rearrangement−Displacement Reactions of Triaryl(halomethyl)silanes with Fluoride and with Alkoxide Ions

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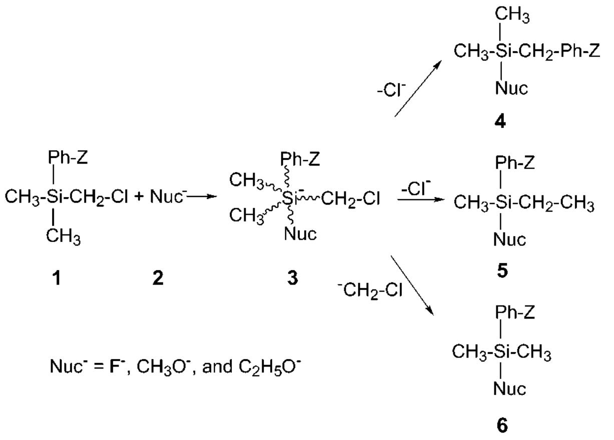
Tetrabutylammonium fluoride (TBAF) reacts with (halomethyl)diphenyl(*para*-substituted-phenyl)silanes (**13**, X = Cl), **14** (X = Br), and **15** (X = I) in ether solvents to give fluorodiphenyl(*para*-substituted-phenylmethyl)silanes (**17a**) and fluorophenyl(phenylmethyl)(*para*-substituted-phenyl)silanes (**20a**) by attack on silicon and migrations of the phenyl or the *para*-substituted-phenyl groups to C-1 with displacement of chloride ion. Sodium methoxide in dioxane effects rearrangement−displacements of **14** (X = Br) to yield methoxydiphenyl(*para*-substituted-phenylmethyl)silanes (**17b**) and methoxyphenyl(phenylmethyl)(*para*-substituted-phenyl)silanes (**20b**). The migratory aptitudes of the varied phenyl groups in rearrangement−displacements of **13** with F^- at 25 °C are *p*-CF_3-Ph, 2.72 > *p*-Cl-Ph, 1.67 > Ph, 1.00 > *p*-CH_3-Ph, 0.91 > *p*-CH_3O-Ph, 0.58 > *p*-$(CH_3)_2N$-Ph, 0.55. For reactions of **14** with sodium methoxide in dioxane, the migratory aptitudes at 23 °C are *p*-CF_3-Ph, 2.53 > *p*-Cl-Ph, 1.64 > Ph, 1.00 > *p*-CH_3O-Ph, 0.84 > *p*-CH_5-Ph, 0.79 > *p*-$(CH_3)_2N$-Ph, 0.68. The migratory aptitudes in the above rearrangement−displacements are increased by electron-withdrawing substituents, and logarithms of the migratory aptitudes give satisfactory linear correlations with σ and/or σ-zero values of the phenyl substituents. Hammett correlations however of the migratory aptitudes from reactions of F^- with **13** (X = Cl) at 0 and −20 °C, **14** (X = Br) at 23, 0, and −20 °C, and **15** (X = I) at 23 °C are not linear. (+)-(Bromomethyl)methyl-1-naphthylphenylsilane (**23**, $[\alpha]_D^{23}$ +8.29°, cyclohexane) reacts with CsF and with TBAF in THF to give benzylfluoromethyl-1-naphthylsilane (**51**, $[\alpha]_D^{25}$ = 0.00°, cyclohexane) and fluoromethyl-(1-naphthylmethyl)phenylsilane (**52**, impure) in 10.4:1 ratio along with unchanged **23** ($[\alpha]_D^{23}$ 8.29°, cyclohexane). Sodium methoxide and (+)-**23** in dioxane at 25 °C and at 0 °C yield (+)-benzylmethoxymethyl-1-naphthylsilane (**64**) and (+)-methoxymethyl(1-naphthylmethyl)phenylsilane (**65**) in ~9:1 ratio. The conversions of (+)-**23** to (+)-**64** occur with >93% inversion about silicon. Reaction of (+)-**23** with sodium methoxide at 25 °C to give (+)-**65** also occurs with inversion. Further, sodium ethoxide and sodium 2-propoxide react with (+)-**23** at 20−25 °C by rearrangement−displacements on silicon with phenyl migrations to yield (+)-benzylethoxymethyl-1-naphthylsilane (**69**) and (+)-benzylmethyl-1-naphthyl-2-propoxysilane (**70**), respectively, each with >95% inversion about silicon. The mechanisms of rearrangement−displacements of **13**−**15** and (+)-**23** by fluoride and by alkoxide ions are discussed.

Fluoride[1] and alkoxide reagents[2] (**2**, Scheme 1) in aprotic environments react with (chloromethyl)silanes **1** by nucleophilic attack on silicon possibly as in **3** to give (1) rearrangement−displacement products **4** and **5** arising from competitive migrations of the phenyl (Ph-Z) and the methyl groups to C-1 with displacement of chloride ion and (2) silyl derivatives **6** by loss of chloromethide ion. The effects of phenyl substituents (Z in Ph-Z) on increasing the rates of disappearance of silanes **1** in reactions with potassium fluoride (**2**, Nuc^- = F^-) in

Scheme 1



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[§] Present address: Pacemaker Inc., Buffalo, NY 21300.

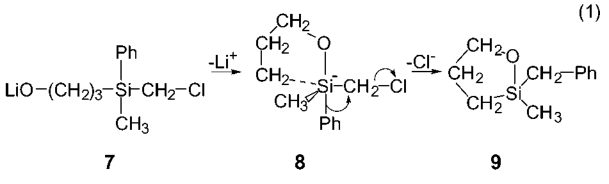
(1) (a) Damrauer, R.; Danahey, S. E.; Yost, V. E. *J. Am. Chem. Soc.* **1984**, *106*, 7633. (b) Damrauer, R.; Yost, V. E.; Danahey, S. E.; O'Connell, B. K. *Organometallics* **1985**, *4*, 1779.

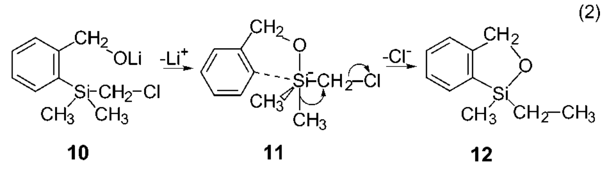
(2) (a) Eaborn, C.; Jeffrey, J. C. *Chem. Ind.* **1955**, 1041. (b) Eaborn, C.; Jeffrey, J. C. *J. Chem. Soc.* **1957**, 137. (c) In reactions of **1** with sodium ethoxide in ethanol, nucleophilic displacements of chloride ion at C-1 also occur by S_N2 processes to give (ethoxymethyl)dimethyl-(substituted-phenyl)silanes. However, in aprotic solvents sodium, potassium, and cesium alkoxides react essentially totally on silicon as in Scheme 1.[2d,e] (d) Sans, E. A. Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1981. (e) Kreeger, R. L.; Menard, P. R.; Sans, E. A.; Shechter, H. *Tetrahedron Lett.* **1985**, *26*, 1115.

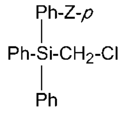
10.1021/jo010471j CCC: $22.00

mesitylene at 85 °C are Z = m-CF_3 > p-Cl > p-F > H > p-CH_3.[1b] In rearrangement−displacements of **1** (Scheme 1) by sodium ethoxide (**2**, $Nuc^- = C_2H_5O^-$) in ethanol at 78 °C, substituents (Z) in the phenyl groups increase the rates of reactions in the order Z = p-Cl > H > p-CH_3 > p-CH_3O.[2a,b] The overall rearrangement−displacement reactions are accelerated when the substituents in the phenyl groups in **1** are electron-withdrawing. The rate-determining steps in the above reactions of **1** have been presumed to involve transition states close in structure to pentacoordinate silylanionic intermediates **3** (Scheme 1) that are stabilized by electron-withdrawing substituents in the phenyl groups.[1b,2a,b]

Of present interest is that the reactions of **1** with potassium fluoride (**2**, $Nuc^- = F^-$) in toluene at 55 °C to yield **4** (Nuc = F) give migratory aptitudes of the phenyl groups in the order Ph > p-CH_3-Ph > m-CF_3-Ph > p-Cl-Ph > p-F-Ph, and the phenyl groups all migrate much more rapidly than do the methyl groups.[1b] Further, the migratory aptitudes in reactions of **1** with sodium methoxide in dioxane at 60 °C to yield **4** (Nuc = CH_3O) are found to be p-CF_3-Ph > m-Cl-Ph > p-Cl-Ph > p-CH_3-Ph > p-CH_3O-Ph > Ph, and the migratory aptitudes of the varied phenyl groups compared to the methyl range from 26 to 5:1.[2d] There are thus no simple interpretations of the electronic effects on migration of the phenyl groups in the rearrangement−displacement processes of **1** as in Scheme 1.[1b,2d] The selectivities and the stereochemistries of rearrangement−displacements of (halomethyl)silanes with nucleophiles[3] including the possibilities of pseudorotation with nucleophiles are also intriguing questions.[2d,3d] An important relevant example of the specificity of rearrangement in reactions of (halomethyl)silanes is cyclization of lithium 3-[(chloromethyl)silyl]-1-propoxide **7** (eq 1) with phenyl migration (>90%) and displacement of chloride ion possibly via **8** to yield oxasilacyclopentane **9**.[4a,b] The ring-closure of [(chloromethyl)dimethylsilyl]-alkoxide **10** at −78 °C in THF takes place, however, by reaction on silicon (eq 2) with rearrangement−displacement involving methyl migration to give oxasilacyclopentane **12** (>90%).[4c] Oxasilacyclopentane **12** is surmized to result upon selective formation and then apical rearrangement-decomposition of the highly strained trigonal bipyramidal intermediate **11**.[4c] Phenyl migration is not observed.[4c−e]







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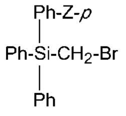

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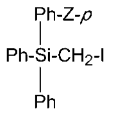
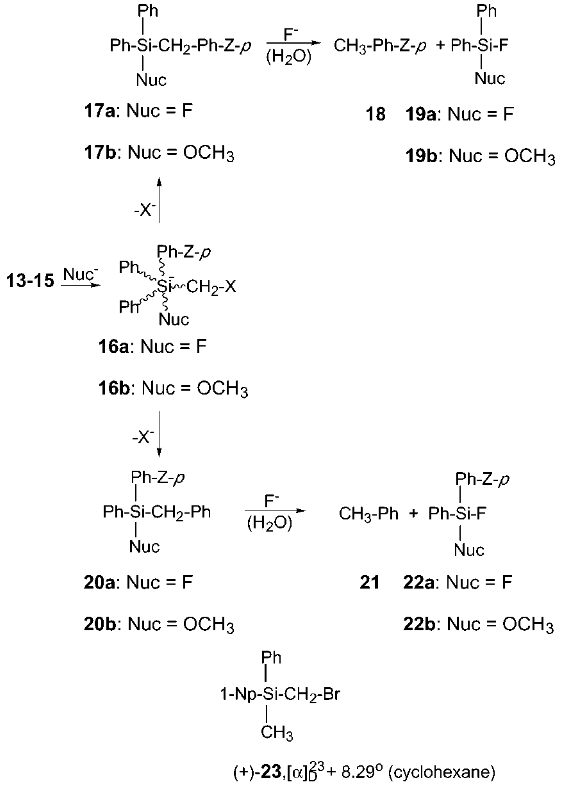


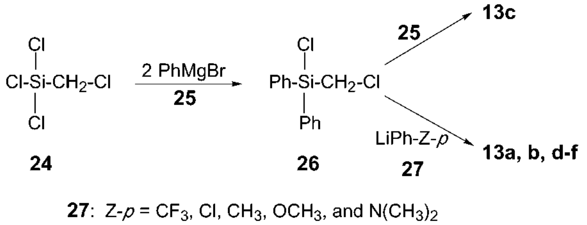
15

13a: Z-p = CF_3	**14a**: Z-p = CF_3	**15a**: Z-p = CF_3
13b: Z-p = Cl	**14b**: Z-p = Cl	**15b**: Z-p = Cl
13c: Z-p = H	**14c**: Z-p = H	**15c**: Z-p = H
13d: Z-p = CH_3	**14d**: Z-p = CH_3	**15d**: Z-p = CH_3
13e: Z-p = OCH_3	**14e**: Z-p = OCH_3	**15e**: Z-p = OCH_3
13f: Z-p = $N(CH_3)_2$	**14f**: Z-p = $N(CH_3)_2$	**15f**: Z-p = $N(CH_3)_2$

Scheme 2



Scheme 3



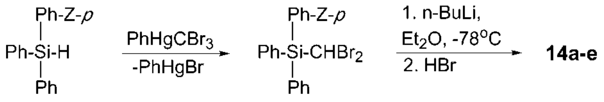
27: Z-p = CF_3, Cl, CH_3, OCH_3, and $N(CH_3)_2$

Studies are now reported of (1) the migratory aptitudes of varied phenyl groups in the reactions of (halomethyl)-silanes **13a**−**f**, **14a**−**f**, and **15a**−**f** with tetrabutylammonium fluoride[5a,b] (TBAF, > 2 equiv) at 25 to −20 °C in THF and of **14a**−**f** with sodium methoxide in dioxane at 23 °C as in Scheme 2 and (2) the stereochemistries of rearrangement−displacement reactions of optically active (bromomethyl)silane **23**[6] with fluoride and with alkoxide reagents in ether solvents at various temperatures. The experiments and results are described as follows.

Results and Discussion

A. Migratory Aptitudes in Rearrangment-Displacement Reactions of Silanes 13−15 with Fluoride Ion. The reactions of fluoride ion with (halomethyl)-silanes **13**−**15** (Scheme 2), synthesized as in Schemes 3 and 4,[7−9] have been investigated in detail. Potassium

Scheme 4

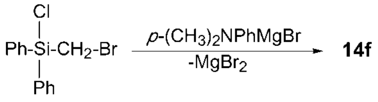


28 **29**

28a: Z-*p* = CF_3; **28b**: Z-*p* = Cl **29a**: Z-*p* = CF_3; **29b**: Z-*p* = Cl

28c: Z-*p* = H; **28d**: Z-*p* = CH_3 **29c**: Z-*p* = H; **29d**: Z-*p* = CH_3

28e: Z-*p* = OCH_3 **29e**: Z-*p* = OCH_3



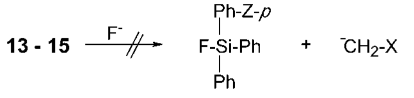
$$\text{Ph-Si(Cl)(Ph)-CH}_2\text{-Br} \xrightarrow[-\text{MgBr}_2]{p\text{-(CH}_3)_2\text{NPhMgBr}} \mathbf{14f} \quad (3)$$

30

$$\mathbf{13a\text{-}e} + \text{KI} \xrightarrow{-\text{KCl}} \mathbf{15a\text{-}e} \quad (4)$$

$$\mathbf{14f} + \text{KI} \xrightarrow{-\text{KBr}} \mathbf{15f} \quad (5)$$

fluoride (KF) and cesium fluoride (CsF) are insoluble in various ether solvents and react slowly with **13**−**15** at −20 to 25 °C. Commercial TBAF[5b] is soluble in THF and is excellent for reactions with **13**−**15**. The behaviors of **13**−**15** with 1 equiv of commercial TBAF in THF are complicated however (Scheme 2) in that rearrangement−displacement products **17a** and **20a** are partly converted to *para*-substituted-toluenes (**18**) and difluorodiphenylsilane (**19a**) and to toluene (**21**) and difluorophenyl (*para*-substituted-phenyl)silanes (**22a**) by reactions with fluoride ion and then H_2O in the reagent. Under proper conditions however, **13**−**15** and TBAF (>2 equiv) yield toluenes **18** and **21** essentially quantitatively upon formation and then cleavage of **17a** and **20a** by fluoride ion followed by protolysis. Displacements of (halomethyl)silanes **13**−**15** by TBAF (eq 6) by attack on silicon to give fluorosilanes **31** and halomethide ion (**32**), and products thereof do not occur. The migratory aptitudes in rearrangement−displacement reactions of **13**−**15** with fluoride ion were determined simply in each experiment from the *para*-substituted-toluene (**18**) and the toluene (**21**) formed as in Scheme 2. The analytical and the statistical methods used are described in the Experimental Section.[10]



(6)

31 **32**

The behaviors of (chloromethyl)silanes **13a**−**f** with TBAF in THF were first studied at 25 °C. The migratory aptitudes (*p*-Z-Ph/Ph) for rearrangements of the varied phenyl groups as in Scheme 2 are summarized in Table 1. The results show that *para*-substituents that are electron-attracting (Z-*p*; CF_3 > Cl) speed whereas those that are usually electron-donating [Z-*p*; $(CH_3)_2N$ > CH_3O > CH_3] slow migration of the phenyl groups. Of note is that the substituent effects on the relative rates of rearrangement of the varied phenyl groups range from 2.72 to 0.55, a factor of only ∼5. The migratory aptitudes in the rearrangement−displacements are interpretable, however, on the basis that the transition states for rearrangement are close in structure to pentacoordinate intermediates **16** (Nuc = F) and/or other polycoordinate silylanionic intermediates as will be discussed and reflect the abilities of the phenyl groups which migrate to remove electrons from silylanionic centers. Further, the Hammett free energy correlations[11,12] obtained upon plotting the logarithms of the migratory aptitudes (ρ-Z-C_6H_4/C_6H_5) against σ (Figure 1a: rho (ρ) = 0.64, corr. coeff. = 0.964, aver. std. deviation ± 0.065) and σ-zero (Figure 1b; ρ = 0.84, corr. coeff. = 0.964, aver. std. deviation ± 0.065) substituent values are satisfactorily linear[12] and consistent with the conclusion that the transition states for rearrangement−displacements in **16** (Nuc = F)[1] or other controlling silylanionic intermediates that are involved are favored at 25 °C by electron-withdrawing substituents in the phenyl groups which migrate.

Reactions of (chloromethyl)silanes **13a**−**f** with TBAF in THF were then investigated at 0 °C and at −20 °C in efforts to spread the migratory abilities of the varied phenyl groups in the rearrangement−displacements (Scheme 2). The yields of **18** and **21** (Scheme 2) in

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(3) (a) For further examples and references to such rearrangement−displacement reactions see ref 1b, 2e, and 3b−f. (b) Corey, J. Y.; Corey, E. R.; Chang, V. H. T.; Hauser, M. A.; Leiber, M. A.; Reinsel, T. E.; Riva, M. E. *Organometallics* **1984**, *3*, 1051. (c) Sans, E. A.; Shechter H. *Tetrahedron Lett.* **1985**, *26*, 1119. (d) Aprahamian, S. L.; Shechter, H. *Tetrahedron Lett.* **1990**, *31*, 1080. (e) Hudrlik, P. F.; Abdallah, Y. M.; Kulkarni, A. K.; Hudrlik, A. M. *J. Org. Chem.* **1992**, *57*, 6552. (f) Eisch, J. J.; Chiu, C. S. *Heteroatom Chem.* **1994**, *5*, 265.

(4) (a) Hudrlik, P. F.; Abdallah, Y. M.; Hudrlik, A. M. *Tetrahedron Lett.* **1992**, *33*, 6743. (b) Oxasilacyclopentane **9** is unstable and was converted by CH_3Li/Et_2O and neutralization to benzyl(3-hydroxy-1-propyl)methylphenylsilane. (c) Hijji, Y. M.; Hudrlik, P. F.; Hudrlik, A. M. *J. Chem. Soc., Chem. Commun.* **1998**, 1213. (d) The importance of steric and strain factors in rearrangement−displacements of halomethylsilanes is illustrated further by reactions of 1-(1-iodoalkyl)-1-phenyl-1-silacyclobutanes with potassium *tert*-butoxide to give 2-alkyl-1-*tert*-butoxy-1-phenyl-1-silacyclopentanes exclusively.[4e] Migrations of the phenyl groups do not occur.[4e] (e) Matsumoto, K.; Miura, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1991**, *32*, 6383.

(5) (a) The migratory aptitudes of various phenyl groups in reactions of **13a**−**f** with fluoride ion were initially studied by Aprahamian, S. L., Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1986, and have been reported in part in ref 3d. (b) Commercial TBAF contains <5% H_2O. The H_2O leads to the silico-protolytic cleavage reactions as in Scheme 2.

(6) Brook, A. G.; Duff, J. M.; Anderson, D. G. *J. Am. Chem. Soc.* **1970**, *92*, 7567.

(7) (a) Smetankina, N. P.; Miryan, N. I. *J. Gen. Chem. USSR* **1967**, *37*, 1309. (b) Belyakova, Z. V.; Golubtsov, S. A. *J. Gen. Chem. USSR* **1961**, *31*, 2966. (c) Motsarev, G. V.; Rosenberg, V. R. *J. Appl. Chem. USSR* **1964**, *37*, 395.

(8) (a) Silanes **14a**,**b**,**d**,**e** were synthesized upon modification of the method for **14c** by Brook, A. G.; Duff, J. M.; Anderson, D. G. *Can. J. Chem.* **1970**, *48*, 561. (b) Silanes **28b**−**e** were obtained as described by Gilman, H.; Dunn, G. E. *J. Am. Chem. Soc.* **1951**, *73*, 3404. Silane **28a** has not been previously reported. (c) The syntheses of **29a**,**b**,**d**,**e** are extensions of that for **29c** by Seyferth, D.; Burtlich, J. *J. Am. Chem. Soc.* **1963**, *85*, 2667 and Seyferth, D.; Burtlich, J.; Dertouzos, H.; Simmons, H. D. *J. Organomet. Chem.* **1967**, *7*, 405.

(9) (a) (Bromomethyl)silane **30** was prepared from (bromomethyl)-trichlorosilane[9b,c] and phenylmagnesium bromide (2 equiv) in Et_2O (see Suppporting Information). (b) Speier, J. L. *J. Am. Chem. Soc.* **1951**, *73*, 826. (c) Khimicheskaya Seriya, *Invest. Akad. USSR.* **1978**, *10*, 2366.

(10) (a) Jones, R. A. *An Introduction to Gas−Liquid Chromatography*; Academic Press: New York, 1970; p 77. (b) Young, H. D. *Statistical Treatment of Experimental Data*; McGraw-Hill: New York, 1962; p 2. (c) The various analyses, experimental errors, standard deviations, statistical details, and the varied attempted correlations of the migratory aptitudes in reactions of **13a**−**f** with F^- are discussed in depth in ref 5a.

(11) (a) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970; Chapter 11, p 347. (b) Exner, O. *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1972, Chapter 1; p 191. (c) Jaffee, H. H. *Chem. Rev.* **1953**, *53*, 191.

(12) Shorter, J. *Correlation Analysis in Organic Chemistry; An Introduction to Linear Free-Energy Relationships*; Clarendon Press: Oxford, 1973; p 105.

Table 1. Migratory Aptitudes of Substituted-Phenyl Groups (*p*-Z-Ph/Ph) in Rearrangement−Displacement Reactions of TBAF with 13a−f in THF at 25°, 0°, and −20 °C, Respectively

13, *p*-Z-Ph-	corrected (*p*-Z-Ph/Ph)[a], 25 °C	corrected (*p*-Z-Ph/Ph)[a], 0 °C	corrected (*p*-Z-Ph/Ph)[a] −20 °C
13a, *p*-CF_3-Ph-	2.72 ± 0.27	3.00 ± 0.30	3.20 ± 0.32
13b, *p*-Cl-Ph-	1.67 ± 0.17	2.01 ± 0.20	2.07 ± 0.20
13c, Ph-	1.00 ± 0.10	1.00 ± 0.10	1.00 ± 0.10
13d, *p*-CH_3-Ph-	0.906 ± 0.091	0.981 ± 0.098	0.974 ± 0.097
13e, *p*-CH_3O-Ph-	0.58 ± 0.12	0.974 ± 0.0970	0.906 ± 0.091
13f, *p*-$(CH_3)_2N$-Ph-	0.550 ± 0.095	1.13 ± 0.17	1.09 ± 0.19

[a] Mean values and the errors in the migratory aptitudes of the various substituted-phenyl groups.

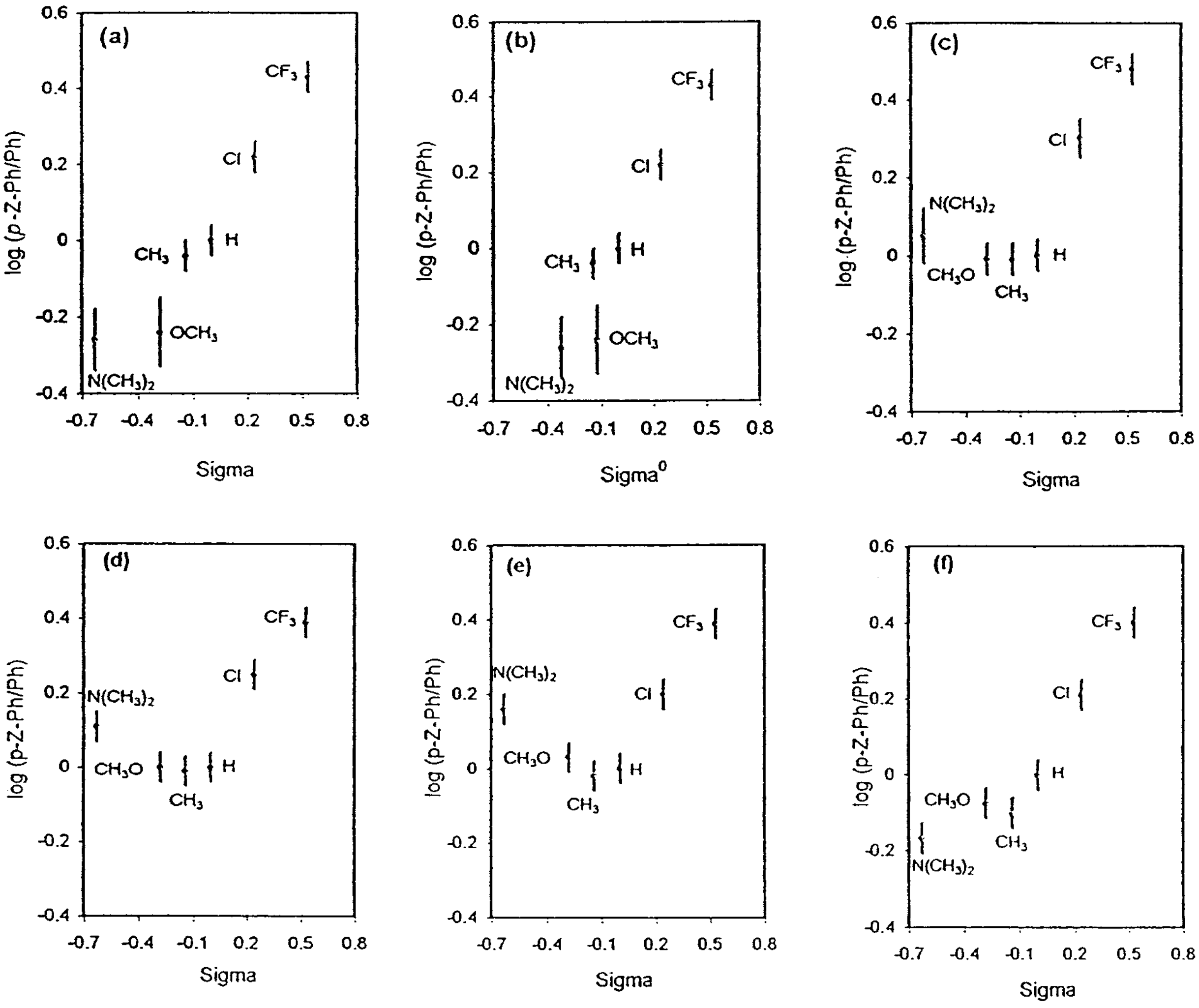


Figure 1. Plots of the logarithms of the migratory aptitudes (*ρ*-Z-Ph/Ph) versus substituent values (*σ* or *σ*-zero) for reactions of (halomethyl)silanes **13a**−**f**, **14a**−**f**, and **15a**−**f** with TBAF or $NaOCH_3$ in the solvent and at the temperature indicated: (a) **13a**−**f**, *σ*, TBAF/THF, 25 °C; (b) **13a**−**f**, *σ*-zero, TBAF/THF, 25 °C; (c) **13a**−**f**, *σ*, TBAF/THF, 0 °C; (d) **14a**−**f**, *σ*, TBAF/THF, 23 °C; (e) **15a**−**f**, *σ*, TBAF/THF, 23 °C; (f) **14a**−**f**, *σ*, $NaOCH_3$, dioxane, 23 °C.

reactions at 0 °C and at −20 °C are ~100%. The migratory aptitudes at 0 °C and −20 °C are listed in Table 1. The study shows, however, that (1) as the reaction temperatures are *lowered*, the spreads in the migratory aptitudes are *reduced* rather than *increased*, (2) the migratory abilities of phenyl groups containing strong electron donors [**13**, Z-*p* = $N(CH_3)_2$ and OCH_3] are *increased* rather than *decreased*, and (3) the *increases* in the migratory aptitudes of phenyl groups substituted by electron-withdrawing substituents (**13**, Z-*p* = CF_3 and Cl) are *small* and probably insignificant statistically. Regression analyses of logarithms of the migratory aptitudes of the phenyl groups versus *σ* constants result in positive *ρ* values (0 °C, $\rho = 0.44$, corr. coeff. = 0.805; −20 °C, $\rho = 0.45$, corr. coeff. = 0.8107) for the rearrangement−displacements but the Hammett plots as in Figure 1c and Supporting Information are curved, and the correlations are deemed to be poor because of mechanism differences rather than experimental errors.[10c,11,12] Strong *para* electron-withdrawing groups increase the migratory aptitudes of phenyl groups in reactions of **13a**−**f** with fluoride ion at all temperatures studied.

The behaviors of (bromomethyl)silanes **14a**−**f** and (iodomethyl)silanes **15a**−**f** with TBAF (2.3 equiv) in THF were studied to determine if there are significant differences in the migratory aptitudes from that for (chloromethyl)silanes **13a**−**f**. In reactions of **14a**−**f** with TBAF at 23 °C phenyl groups with electron-withdrawing *para*-substituents (Z-*p* = CF_3 and Cl) again migrate significantly faster (Table 2) than phenyl. When the *para*-

Table 2. Migratory Aptitudes of Substituted-Phenyl Groups (*p*-Z-Ph/Ph) in Rearrangement−Displacement Reactions of TBAF in THF with 14a−f at 23, 0, and −20 °C, Respectively, and 15a−f at 23 °C

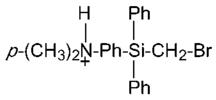
14 or **15**, *p*-Z-Ph-	corrected (*p*-Z-Ph/Ph),[a] 23 °C	corrected (*p*-Z-Ph/Ph),[a] 0 °C	corrected (*p*-Z-Ph/Ph),[a] −20 °C
14a, *p*-CF_3-Ph-	2.43 ± 0.24	2.77 ± 0.28	2.96 ± 0.30
14b, *p*-Cl-Ph-	1.79 ± 0.18	1.92 ± 0.19	1.96 ± 0.20
14c, Ph-	1.00 ± 0.10	1.00 ± 0.10	1.00 ± 0.10
14d, *p*-CH_3-Ph-	0.967 ± 0.097	0.96 ± 0.10	0.97 ± 0.10
14e, *p*-CH_3O-Ph-	1.00 ± 0.10	1.05 ± 0.11	0.97 ± 0.10
14f, *p*-$(CH_3)_2N$-Ph-	1.30 ± 0.13	1.34 ± 0.13	1.36 ± 0.14
15a, *p*-CF_3-Ph-	2.46 ± 0.25		
15b, *p*-Cl-Ph-	1.65 ± 0.17		
15c, Ph-	1.00 ± 0.10		
15d, *p*-CH_3-Ph-	0.96 ± 0.10		
15e, *p*-CH_3O-Ph-	1.07 ± 0.10		
15f, *p*-$(CH_3)_2N$-Ph-	1.43 ± 0.14		

[a] Mean values and the errors in the migratory aptitudes of the various substituted-phenyl groups at the indicated temperatures.

substituents are electron-donating (Z-*p* = CH_3 and OCH_3) the migratory aptitudes of the substituted phenyl groups are essentially the same as for phenyl. For **14f** [Z-*p* = $N(CH_3)_2$], however, the migratory aptitude of the *p*-dimethylaminophenyl group is somewhat larger than for the phenyl group. The Hammett plot in Figure 1d thus does not give a satisfactory linear correlation.[11,12] The *p*-dimethylamino group does not behave simply as an electron donor in the migrations in reactions of **14f** with fluoride ion.

The effects of solvents and experimental differences on rearrangement−displacements of **14f** by fluoride ion at 23 °C were then studied. The migratory aptitude of the *p*-dimethylaminophenyl group in reactions of **14f** with TBAF in dioxane (1.24) is similar to that in THF (1.30, Table 2). Further, with **14f** and TBAF in 96% hexane−4% THF, the migratory aptitude of the *p*-dimethylaminophenyl group is 1.66. There is thus no large effect of solvent on the migratory aptitude of the *p*-dimethylaminophenyl group, but the group migrates faster than phenyl, *p*-tolyl, or *p*-anisyl under identical conditions.

The effects of concentration of fluoride ion on the migratory aptitudes in rearrangement−displacements of **14b** and of **14f** in THF at 23 °C were also investigated. The migratory aptitudes from these experiments are summarized in Supporting Information. For **14b**, increasing the fluoride ion concentration from 0.095 to 2.44 M causes little change in the migratory aptitude of the *p*-chlorophenyl group. Raising the TBAF from 0.004 to 2.44 molar in reactions of **14f**, however, results in an increase in the migratory aptitude of the *p*-dimethylaminophenyl group from 1.23 to 1.51. That the migratory ability of the *p*-dimethylaminophenyl group increases with TBAF equivalents raises the possibility that the fluoride reagent contains acid (HF) which converts **14f** extensively to its ammonium salt **33**. Thus in rearrangement−displacements of **33** by fluoride ion containing acid the *p*-dimethylammoniumphenyl group will be relatively highly electron-deficient and be expected to migrate with its electrons more readily than phenyl. To evaluate that rearrangement−displacements might have involved **33**, reactions of **14f** with TBAF (3 equiv) were conducted in the presence of excess tributylamine (3.5 equiv). The purpose of the tributylamine was to deprotonate the possible **33** present to **14f**. The migratory aptitude for the "*p*-dimethylaminophenyl group" in the above experiment is 1.37 and therefore similar to that for **14f** in the absence of the proton scavenger base, tributylamine. Rearrangement−displacement of **33** by fluoride ion in the above experiment is not likely.



$p\text{-}(CH_3)_2\overset{H}{\underset{+}{N}}\text{-Ph-}\overset{Ph}{\underset{Ph}{Si}}\text{-}CH_2\text{-Br}$

33

The migratory aptitudes in reactions of **14f** in dioxane at 23 °C with TBAF (3 equiv) in the presence of sodium methoxide (16 equiv) were determined. The migratory aptitude for the *p*-dimethylaminophenyl group is 1.19 and similar to that (1.24) for **14f** with TBAF in dioxane. Since TBAF effects complete rearrangement−displacement of **14f** in less than 3 min whereas ~36 h are necessary for sodium methoxide, **14f** in the presence of the fluoride and methoxide reacts essentially totally with fluoride ion. The sodium methoxide ensures that **14f** is not converted to **33** which then undergoes rearrangement−displacements as in Scheme 2 or related processes. Reactions of **14f** were also effected with CsF in THF. Although highly insoluble, CsF (9.5 equiv) reacts effectively with **14f** in THF at 23 °C and results in a migratory aptitude of the *p*-dimethylaminophenyl group of 1.63.

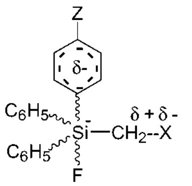
The rearrangement−displacement behaviors of (bromomethyl)silanes **14a**−**f** with TBAF (2.3 equiv) in THF were then investigated at 0 °C and −20 °C (Table 2). Lowering the reaction temperatures does not affect the migratory aptitudes of the phenyl groups greatly. Plots (see Supporting Information) of the logarithms of the migratory aptitudes (*p*-Z-Ph/Ph) at 0 °C and at −20 °C versus σ-zero values are not satisfactorily linear and are similar to that in Figure 1d for reactions at 23 °C. The acceleration of the migratory aptitude by the *p*-$(CH_3)_2N$ group continued to be of interest.

The rearrangement−displacement reactions of (iodomethyl)silanes **15a**−**f** with fluoride ion (2.3 equiv) were also studied (Scheme 2) in THF at 23 °C. The TBAF reagent converts **15a**−**f** (Scheme 2) quantitatively to *para*-substituted-toluenes (**18**) and toluene (**21**). The rearrangement−displacement results (Table 2) show trends essentially identical to those for **13a-f** and **14a**−**f**. The plot (Figure 1e) of the logarithms of the migratory aptitudes in Table 2 versus appropriate σ-zero substituent values is curved. The overall behaviors of (halomethyl)silanes **13a**−**f**, **14a**−**f**, and **15a**−**f** with fluoride in THF are thus similar. The questions of concern are (1) why are the attempted free energy correlations nonlinear, (2) what are the mechanisms of rearrangement−displacements of **13a**−**f**, **14a**−**f**, and **15a**−**f** by fluoride ion, and

(3) why does the *p*-dimethylaminophenyl group migrate as rapidly as found.

The Hammett equation assumes that the reaction constant, rho (ρ), is independent of sigma (σ) or sigma-zero ($\sigma°$) substituent constants.[11,12] Curved Hammett plots are theorized to arise because the requirements for breaking bonds in a series of intermediates as in **16** (Nuc = F, Scheme 2) are not constant and ρ is σ constant dependent ($\rho = \rho_o + \tau\sigma$ in which ρ_o is the reaction constant independent of the substituent and τ is dependent on the structure of the reaction center and reflects the difference between transition state and ground-state effects).[13] On the basis that the ρ values for the observed relative migratory aptitudes in reactions of **13a−f** with fluoride ion are σ constant dependent, second-order least-squares regressions result in calculated values for ρ for substituted phenyl groups at 0 °C (corr. coeff. = 0.971) and −20 °C (corr. coeff. = 0.976) as follows: p-CF_3-C_6H_4, 0.85, 0.92; p-Cl-C_6H_4, 0.65, 0.70; C_6H_5, 0.47, 0.52; p-CH_3-C_6H_4, 0.37, 0.41; p-CH_3O-C_6H_4, 0.27, 0.31; p-$(CH_3)_2N$-C_6H_4, 0.03, 0.04. The results are (1) the free energy correlation lines are still curved, (2) the calculated ρ values are all greater than zero and in agreement with expectations that transition states such as from **16** (Nuc = F) are always negative (silicanionic), and (3) as the σ constants get larger, the calculated ρ values and the electronic demands during rearrangement decrease.

The electrical effects on the migratory aptitudes and the satisfactory and the deviant free energy correlations for rearrangement−displacements of **13−15** by F^- at various temperatures are consistent, however, with the presumption that there are differences in the transition states of the pentacoordinate silicanionic processes as in **34−36**. In **34−36** fluorine and the migrating phenyl group are apical, displacement occurs on silicon with inversion, and halogen is expelled by backside attack of the migrating phenyl group on carbon of the equatorial halomethyl substituent. As the lengths of the carbon−halogen bonds in **34−36** increase, the transition states become more neutral as in **35**, and the electronic demands from the phenyl substituents during rearrangment are lowered. Further, when there is greater heterolytic breaking of a C−X bond as in **36** in which Z is highly electron donating (Z = $N(CH_3)_2$ or OCH_3), the greater is the electronic compensation by participation of the migrating phenyl group.



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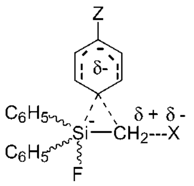

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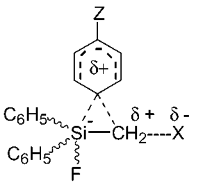

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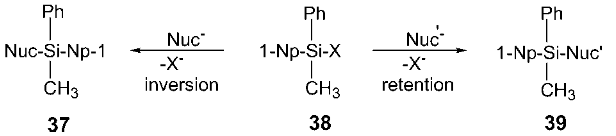
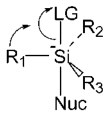
Scheme 5



Although the behaviors of **13−15** with F^- can be rationalized as in **34−36**, the linear and the unsatisfactory Hammett correlations obtained might have origins quite different than as proposed above. The stereochemistries of nucleophilic displacements on silicon can be complicated, much more so than on carbon. Of relevance is that chiral tertiary silanes undergo bimolecular displacements by nucleophiles with complete retention or inversion[14] as in Scheme 5 or to give substitution products which are partly or totally racemic.[14] Displacements with inversion on silicon are usually presumed to involve transition states from distorted trigonal bipyramidal intermediates **40** involving backside attack in which the entering (Nuc) and leaving groups (LG) are both apical.[14] In substitution processes resulting in retention in stereochemistry it has been theorized that (1) the incoming nucleophile enters equatorially as in **41**, the leaving group is expelled axially, and the nucleophile takes the position initially occupied by the leaving group, (2) the entering nucleophile attacks from an axial position as in **42** with equatorial displacement of the leaving group and the nucleophile taking its place, or (3) reaction occurs as in **43−45** (Figure 2) in which the incoming nucleophile is axial and the leaving group is equatorial, pseudorotation occurs in which the nucleophile becomes equatorial and the group to depart is axial, and then the leaving group is expelled.[14] Partial or total racemization can occur upon extension of the pseudorotational processes.[14] Further possibilities include attack of nucleophiles on **40−42** to give dinegatively charged hexacoordinate intermediates (or transition states) such as **46−48** and/or their isomers[14] that lose their leaving groups and a nucleophile to give displacement products with retention (**39**), inversion (**37**), or partial or total racemization.



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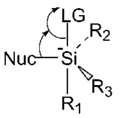

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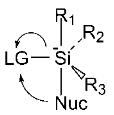

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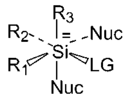

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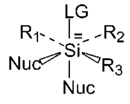

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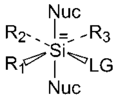

48

In the rearrangement−displacement reactions of (halomethyl)silanes with F^- as in Scheme 2 or if there is attack on silicon as in **40−48** et al. in such processes, backside attack of the migrating group on carbon (C-1) from which the leaving group is expelled is expected.[15] What the stereochemistries will be, however, at the silyl centers in the rearrangement−displacement acts in **13−15** are not obvious.[14] Of further concern are the differ-

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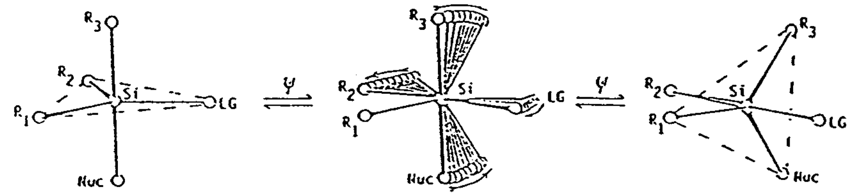
(13) (a) Swain, C. G.; Langsdorf, W. P. *J. Am. Chem. Soc.* **1951**, *73*, 2813. (b) Westaway, K. C.; Waszczylo, Z. *Can. J. Chem.* **1982**, *60*, 2500.

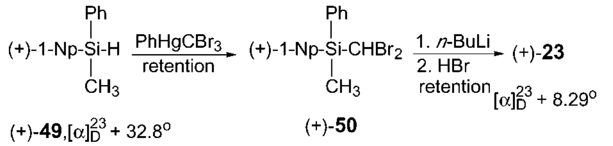
(14) The stereochemistries of displacement reactions of silanes by nucleophiles and formation, fluxional behavior, and pseudorotation of silylanionic complexes have been reviewed in (a) *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y. J., Eds.; Wiley & Sons: Chichester, 1998 by (1) Bassindale, A. R.; Glynn, S. J.; Taylor, P. G., Chapter 9, p 495 and (2) Kost, D.; Kalikhman, I., Chapter 23, p 1339, (b) Chuit, C.; Corriu, J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371, (c) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17, (d) *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z. J., Eds.; Wiley & Sons: Chichester, 1989 by (1) Corey, J. Y., Chapter 1, p 1, (2) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E., Chapter 3, p 305, (3) Bassindale, A. R.; Taylor, P. G., Chapter 13, p 839, and (4) Corriu, R. J. P.; Young, J. C., Chapter 20, p 1289, and (e) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231.



43 **44** **45**

Figure 2. Pseudorotation in trigonal bipyramidal silicon intermediates **43** and **45**. In **43** groups R_1, R_2, and LG are equatorial, and R_3 and Nuc are axial. In **45**, R_1, R_3, and Nuc are equatorial, and R_2 and LG are axial. Group R_1 is the pivot in the pseudorotational processes.

Scheme 6

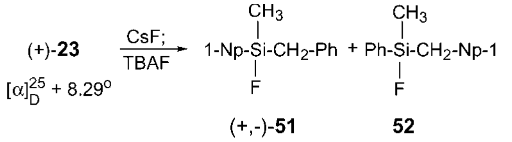


$$(+)\text{-1-Np-}\underset{CH_3}{\overset{Ph}{Si}}\text{-H} \xrightarrow[\text{retention}]{PhHgCBr_3} (+)\text{-1-Np-}\underset{CH_3}{\overset{Ph}{Si}}\text{-CHBr}_2 \xrightarrow[\text{2. HBr; retention}]{\text{1. }n\text{-BuLi}} (+)\text{-}\mathbf{23}\ [\alpha]_D^{23}+8.29^\circ$$

(+)-**49**, $[\alpha]_D^{23}$ + 32.8° (+)-**50**

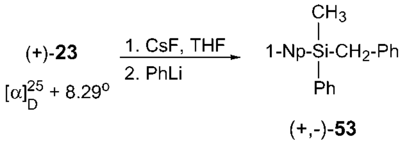
ences in the reaction mechanisms when the migratory aptitudes and the free energy correlations change as has now been found. In efforts to clarify some of the above questions, the stereochemical behavior of (+)-**23** with fluoride ion has been investigated.

B. Study of the Stereochemistry of Reactions of (+)-23 with Fluoride Ion. Silane (+)-**23** ($[\alpha]_D^{23}$ + 8.29°, cyclohexane),[6] prepared as in Scheme 6,[16a,b] reacts quickly (2−3 min) in THF with TBAF and with CsF (heterogeneous, 9 h) at 20−25 °C as in eq 7 to give, after rapid workup and chromatography of the reaction products on silica gel, optically inactive benzylfluorosilane **51** $[\alpha]_D^{25}$ = 0.00°, cyclohexane; 28%)] and impure fluoro-(1-naphthylmethyl)silane **52**. As a check of its lack of optical activity, crude **51**, as obtained from (+)-**23** and CsF in THF at 23 °C with minimum handling, was treated with phenyllithium (eq 8).[17] Optically inactive benzylsilane **53** ($[\alpha]_D^{25}$ = 0.00°, cyclohexane) was obtained.[17] To verify its structure (+,−)-benzylfluorosilane **51** was synthesized (eq 9) from (+,−)-benzylmethoxysilane **54**[18] and BF_3 etherate. From experiments in which (+)-**23** reacts with TBAF (2 equiv) at 25 °C in THF and the **51** and **52** formed are protolytically cleaved by TBAF/H_2O to **21** and 1-methylnaphthalene (1-CH_3-Np), respectively, the migratory aptitudes for the phenyl and the 1-naphthyl groups as in eq 7 are ~10.4:1.[19] Since fluorosilane **52**, the product of 1-naphthyl migration, is obtained only in small quantities from (+)-**23** and does not chromatograph well, its optical properties could not be determined accurately. In reactions with TBAF or CsF in THF in which (+)-**23** ($[\alpha]_D^{25}$ + 8.29°, cyclohexane) is in excess, the recovered (bromomethyl)silane (+)-**23** is not changed stereochemically. Silane (+)-**23** is not racemized prior to or during its rearrangement−displacement reactions with fluoride ion.



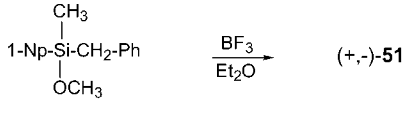
$$(+)\text{-}\mathbf{23}\ [\alpha]_D^{25}+8.29^\circ \xrightarrow[\text{TBAF}]{\text{CsF;}} \text{1-Np-}\underset{F}{\overset{CH_3}{Si}}\text{-CH}_2\text{-Ph} + \text{Ph-}\underset{F}{\overset{CH_3}{Si}}\text{-CH}_2\text{-Np-1} \quad (7)$$

(+,-)-**51** **52**



$$(+)\text{-}\mathbf{23}\ [\alpha]_D^{25}+8.29^\circ \xrightarrow[\text{2. PhLi}]{\text{1. CsF, THF}} \text{1-Np-}\underset{Ph}{\overset{CH_3}{Si}}\text{-CH}_2\text{-Ph} \quad (8)$$

(+,-)-**53**



$$\text{1-Np-}\underset{OCH_3}{\overset{CH_3}{Si}}\text{-CH}_2\text{-Ph} \xrightarrow[Et_2O]{BF_3} (+,-)\text{-}\mathbf{51} \quad (9)$$

(+,-)-**54**

In a further attempt to obtain **51** with optical activity, (+)-**23** ($[\alpha]_D^{23}$ + 8.29°, cyclohexane) in THF was treated with TBAF (1 equiv) in THF for 10 s (or less) at room temperature. The mixture was immediately diluted, rapidly cooled by addition of cold pentane (−78 °C), and then filtered quickly to remove the TBABr and the TBAF precipitated. Rapid concentration of the cold reaction solution at reduced pressure followed by rapid chromatography on silica gel gave a mixture of (+)-**23** and **51** with an observed rotation of α_D^{25} = +0.100° (cyclohexane) as the major product. The product was shown by ^1H NMR to be a 1:4 mixture of **23** and **51**, and therefore its optical activity is due to initial (+)-**23**.

Experiments were then executed with TBAF and excess (+)-**23** as in eq 7 in which the times for rearrangement−displacements of the (+)-**23**, exposure of the **51** and **52** formed to F^-, and handling of the reaction mixtures were greatly minimized The optical properties of the **51** formed were then estimated as quickly as practical without the product being separated from the reaction solutions. Reactions were conducted in 5−10 min in THF at 23 °C in which the equivalents of (+)-**23** ($[\alpha]_D^{23}$ +8.29°, cyclohexane) to TBAF ranged from 1.0 to 0.25−0.98 [(+)-**23** was always in excess], the solutions were then rapidly filtered and quickly diluted to volume, and their optical rotations were immediately determined

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(15) Larson, G. L.; Klesse, R.; Cartledge, F. K. *Organometallics* **1987**, *6*, 2250 report that thermolysis of (*S*,*S*)-(1-chloroethyl)methyl(1-naphthyl)phenylsilane at 280 °C results in rearrangements in which the phenyl and the 1-naphthyl groups migrate from silicon by backside processes (95%) resulting in inversion about C-1 of the 1-chloroethyl group along with migrations of chlorine to silicon to yield chlorosilanes in which the stereochemistry about silicon is racemic. The mechanism by which loss of stereochemistry about silicon occurs has not been established.

(16) (a) Sommer, L. H.; Fyre, C. L.; Parker, G. A.; Michael, K. W. *J. Am. Chem. Soc.* **1964**, *86*, 3271. (b) Sommer, L. H.; Ulland, L. A.; Parker, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 3469.

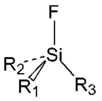
(17) (a) Chiral *tert*-fluorosilanes undergo bimolecular displacement by aryllithium reagents to give substitution products with high-order retention in stereochemistry.[17b−d] (b) Sommer, L. H.; Korte, K. D.; Rodewald, P. G. *J. Am. Chem. Soc.* **1967**, *89*, 862. (c) Sommer, L. H.; Rodewald, P. G. *J. Am. Chem. Soc.* **1967**, *89*, 5802. (d) Corriu, R. J. P.; Royo, G. *Bull. Soc. Chem. Fr.* **1972**, 1497.

(18) (+,−)-Methoxysilane **54** was prepared by rearrangement−displacement reaction of (+,−)-**23** with sodium methoxide in THF.

(19) Reaction of (+,−)-**51** with TBAF (1 equiv) gives **21** quantitatively and presumably difluoromethyl-1-naphthylsilane. With additional TBAF conversion of the difluoromethyl-1-naphthylsilane to naphthalene occurs. Similarly, **52** is converted by excess TBAF to 1-methylnaphthalene and to benzene.

without further workup. As detailed in Supporting Information, what is learned from these experiments is that the optical rotations of the reaction mixtures before any workup correspond quite well to the (+)-**23** expected to be present, and the contributions of **51** to the optical activities are nonexistent or at best small. Further, rapid workup of the reaction mixture from (+)-**23** and TBAF in a 1.00:0.25 mole ratio reveals that the **51** in the product is optically inactive.

From the above experiments with (+)-**23** and F^- it cannot be concluded whether the optically inactive **51** is formed during or/and after rearrangement−displacements. Fluorosilanes such as **55** are known to react with fluoride donors (metal fluorides, ammonium fluoride, and tetraalkylammonium fluorides) in protic, aprotic, crown ether, or (best) cryptand environments to give the corresponding difluorosilicate ions **56**.[14b,20] Difluorosilicate ions such as $Ph_3SiF_2^-$,[20a,d,f,h] 1-$NpPh_2SiF_2^-$,[20b] $Ph_2(CH_3)SiF_2^-$,[20h] and $(CH_3)_3SiF_2^-$ [20c,e] have trigonal pyramidal structures as in **56** in which the fluorines, the most electronegative substituents, are in the axial positions. Silicanions such as **56** will be optically inactive.[20] In the present experiments, if reactions of (+)-**23** with F^- were to give optically active **51** and then addition of F^- to the **51** to form difluorosilicate ion **57** occurs rapidly and reversibly, racemic **51** will be the product. In support of such a possibility for racemization of (+)-**23** by F^-, (−)-fluoromethyl-1-naphthylphenylsilane (**58**, a close analogue of (+)-**23**)[20] in THF has been presently found to rapidly lose its optical activity completely possibly via **59** upon exposure to TBAF at room temperature (see Experimental Section).[21] The questions thus still remain as to whether the (+,−)-**51** obtained from (+)-**23** and F^- results from (1) racemization of optically active **51** via pentacoordinate intermediate **57**[21e] (or/and its hexacoordinate derivatives), (2) rearrangement−displacement of pentacoordinate silylanionic intermediates such as **60** in which there has been racemizing pseudorotation,[21e] or/and (3) formation and decomposition of optically inactive hexacoordinate silyldianionic intermediates such as **61**. The stereochemical behavior of (+)-**23** or other chiral (halomethyl)silanes, and their products with F^- at very low temperatures, possibly shorter reaction times, and using better rapid techniques, will have to be studied to answer the above questions. In efforts to clarify the mechanisms of rearrangement−displacement reactions of (halomethyl)silanes with other nucleophiles,[2d,f] the behaviors of **14** and (+)-**23** with alkoxides in aprotic environments have been investigated.



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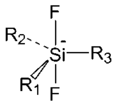

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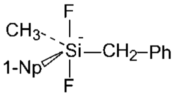

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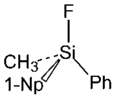

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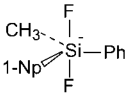

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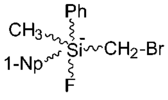

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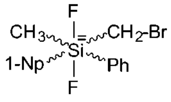

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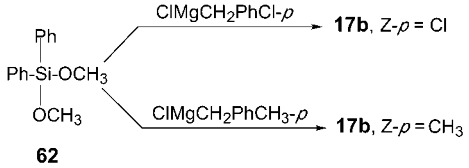
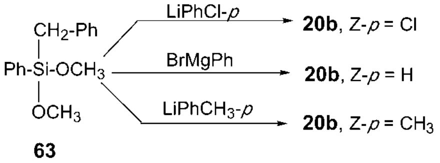
C. Migratory Aptitudes in Rearrangement−Displacement Reactions of Silanes 14 with Sodium Methoxide. Study has been made of the migratory aptitudes in rearrangement−displacements of **14a**−**f** with sodium methoxide (Scheme 2, $Nuc^- = CH_3O^-$, 10−12 equiv) in dioxane and in THF at 23 °C. Sodium methoxide reacts slowly with **14** by attack on silicon (Scheme 2) to give methoxysilanes **17b** and **20b**, presumably upon formation and collapse of pentacoordinate silylanionic intermediates **16b** or (less likely) related hexacoordinate anionic intermediates. Rearrangement−displacement products **17b** (Z-*p* = Cl and CH_3) and **20b** (Z-*p* = Cl, H, and CH_3) were synthesized from dimethoxysilanes **62**[22a,b] and **63**, respectively, as in Schemes 7 and 8 (see Supporting Information).

Scheme 7



Scheme 8



Gas chromatographic analyses of reaction mixtures from **14f** and sodium methoxide in dioxane at 23 °C reveal that the initial rearrangement−displacement products, **17b** [Z-*p* = $(CH_3)_2N$] and **20b** [Z-*p* = $(CH_3)_2N$], are converted in part to *p*-dimethylaminotoluene [**18**, Z-*p* =

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[20] (a) Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490. (b) Harland, J. J.; Payne, J. S.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987**, *26*, 760. (c) Scherbaum, F.; Huber, B.; Muller, G.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1542. (d) Damrauer, R.; O'Connell, B.; Danahey, S. E.; Simon, R. *Organometallics* **1989**, *8*, 1167. (e) Dixon, D. A.; Farnham, W. B.; Heilemann, W.; Mewa, R.; Noblemeyer, M. *Heteroat. Chem.* **1993**, *4*, 287. (f) Pilcher, A. S.; Ammon, H. L.; DeShong, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 5166. (g) Albanese, D.; Landini, D.; Penso, M. *Tetrahedron Lett.* **1995**, *36*, 8865. (h) Yamaguchi, S.; Akiyama, S.; Tamoa, K. *Organometallics* **1999**, *18*, 2851.

[21] (a) (−)-Fluorosilane **58** has been prepared from (−)-[(−)-menthoxy]methyl-1-naphthylphenylsilane and BF_3 in Et_2O by Sommer, L. H.; Frye, C. L.; Parker, G. A.; Michael, K. W. *J. Am. Chem. Soc.* **1964**, *86*, 3271. (b) (−)Silane **58** has also been obtained[21c] by treating (−)-bromo(methyl)-α-naphthylphenylsilane in $CHCl_3$ (11.5 mL) with solid cyclohexylammonium fluoride at room temperature as follows. Upon immediately stirring the mixture for a few seconds the fluoride salt dissolved. The reaction system was immediately quenched by rapid addition of pentane (200 mL) cooled to ∼−78 °C. The (−)-**58** isolated was obtained in 96.2% yield, 92% optically pure with 96% net inversion of configuration.[21c] (c) Sommer, L. H.; Parker, G. A.; Lloyd, N. C.; Frye, C. L.; Michael, K. W. *J. Am. Chem. Soc.* **1967**, *89*, 857. (d) The above techniques for synthesis of (−)-**58**[21b,c] are essentially identical to those presently used with (+)-**23** and TBAF for 10 s (or less). (e) The rate constants and the probable reaction mechanisms for racemization of dilute solutions of **58** (0.047 M) by cyclohexylammonium fluoride (5×10^{-6} to 1×10^{-4} M) at 24.4 °C in CCl_4 containing alcohols in various (small) concentrations have been studied by Sommer, L. H.; Bauman, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 7045.

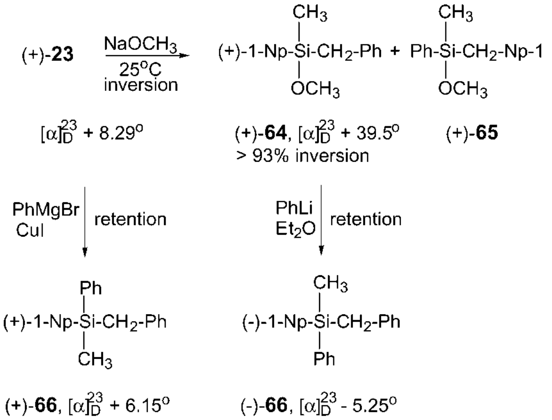
[22] (a) Hiratsuka, K. Jpn. Pat. 5330, Sept. 15, 1951; *Chem. Abst.* **1953**, *47*, 9345. (b) Tacke, R.; Strecker, M.; Sheldrick, W. S.; Heeg, E.; Berndt, B.; Knapstein, K. M. Z. *Naturforsch. Teil B* **1979**, *34B*, 1279.

Table 3. Migratory Aptitudes of Substituted-Phenyl Groups (*p*-Z-Ph/Ph) in Rearrangement−Displacements of 14a−f with Sodium Methoxide in Dioxane at 23 °C

14, *p*-Z-Ph-	corrected (*p*-Z-Ph/Ph)[a]	**14**, *p*-Z-Ph-	corrected (*p*-Z-Ph/Ph)[a]
14a, *p*-CF_3-Ph-	2.53 ± 0.25	**14d**, *p*-CH_3-Ph-	0.79 ± 0.08
14b, *p*-Cl-Ph-	1.64 ± 0.16	**14e**, *p*-CH_3O-Ph-	0.84 ± 0.08
14c, Ph-	1.00 ± 0.10	**14f**, *p*-$(CH_3)_2N$-Ph-	0.68 (0.69)[b] ± 0.07

[a] Mean values of the migratory aptitudes of the various substituted-phenyl groups. [b] The migratory aptitude from reaction of **14f** with sodium methoxide in THF at 23 °C.

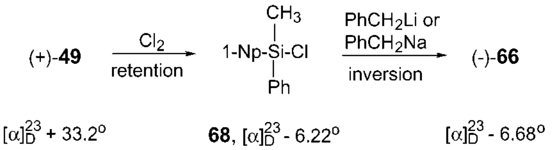
Scheme 9



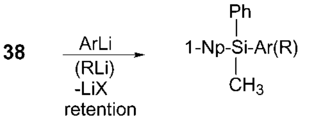
$(CH_3)_2N$] and toluene (**21**). Fluoride ion, however, is excellent for cleaving methoxysilanes **17b** and **20b**. Excess TBAF (2.3 equiv) was thus added to each reaction mixture from **14a**−**f** and sodium methoxide after TLC revealed total depletion of the initial halides by the sodium methoxide. The reaction mixtures were then worked up for toluenes **18** and **21** as previously described. The experimental results are highly reproducible and the migratory aptitudes determined are summarized in Table 3. This study shows that (1) substituent effects on the migratory aptitudes are small, (2) *para* electron-withdrawing substituents (Z-*p* = CF_3 and Cl) accelerate rearrangements of phenyl groups, (3) *p*-$(CH_3)_2N$, *p*-CH_3O, and *p*-CH_3 substituents behave as traditional electron-donors with respect to migratory aptitudes, and (4) the migratory ability of the *p*-dimethylaminophenyl group in reactions of **14f** with methoxide ion is approximately half that with fluoride ion. Of particular note is that the Hammett plot (Figure 1f) of logarithms of the migratory aptitudes and σ-zero substituent values for rearrangement−displacement reactions of **14a**−**f** with methoxide ion has a ρ value of 0.72 with a correlation coefficient of 0.97, is more linear than for such reactions of **14a**−**f** with fluoride ion, and is clearly satisfactory.[12] The behaviors of **14a**−**f** with methoxide ion appear simpler than with fluoride ion.

D. The Stereochemistries of Reactions of (+)-23 with Alkoxide Ions. The stereochemistries of reactions of (+)-**23** with alkoxide reagents have been studied as follows. Bromomethylsilane (+)-**23** ($[\alpha]_D^{23}$ +8.29°, cyclohexane) reacts with sodium methoxide (1.0 equiv) in dioxane by rearrangement−displacements (Scheme 9) at 25 °C to yield (+)-benzylmethoxysilane **64** ($[\alpha]_D^{23}$ +39.5°, cyclohexane) and (+)-methoxy(1-naphthylmethyl)silane **65** in ∼9.5:1 ratio.[23] The behavior of (+)-**23** with sodium methoxide/dioxane at 0 °C to give (+)-**64** ($[\alpha]_D^{23}$ + 38.8°, cyclohexane) and (+)-**65** is essentially identical to that at 25 °C. Silanes (+)-**64** and (+)-**65**, products of phenyl and 1-naphthyl migrations, respectively, were identified from their analyses and spectra, and/or upon comparison with authentic racemic samples (see Experimental Section).[24]

Scheme 10



The stereochemistry of phenyl migration in rearrangement−displacement of (+)-**23** to yield (+)-**64** was determined from results summarized in Scheme 9. First, methoxysilane (+)-**64** (Scheme 9) is converted by phenyllithium in Et_2O to the displacement product, (−)-benzylphenylsilane **66** ($[\alpha]_D^{23}$ −5.25°, cyclohexane). Since all previous chiral alkoxysilanes including **38** (X = OR, eq 10) react with aryllithium and alkyllithium reagents in ether solvents to give displacement products **67** with retention of configuration,[16a,17c] (−)-**66** is concluded to be formed (Scheme 9) from (+)-**64** and phenyllithium with retention. Correlation of the stereochemistry of (−)-**66** with (+)-**23** was then accomplished upon reaction of (+)-**23** with phenylmagnesium bromide (Scheme 9) in the presence of cuprous iodide to give (+)-**66**, $[\alpha]_D^{23}$ + 6.15° (cyclohexane). Since no silicon−carbon bonds are broken in the coupling reaction of (+)-**23** with phenylmagnesium bromide and cuprous iodide, (+)-**66** is formed with retention of configuration. Therefore, for conversion of (+)-**49** to (−)-**66** as in Schemes 6 and 9, reaction of (+)-**23** with sodium methoxide to give (+)-**64** must occur with >93% inversion on silicon.



$$\mathbf{38}\ \xrightarrow[\substack{-\text{LiX} \\ \text{retention}}]{\substack{\text{ArLi} \\ \text{(RLi)}}}\ \text{1-Np-}\overset{\text{Ph}}{\underset{\text{CH}_3}{\text{Si}}}\text{-Ar(R)} \qquad (10)$$

67

The stereochemical conclusion for conversion of (+)-**23** to (−)-**66** as in Scheme 9 is also consistent with observations (Scheme 10) that (1) chlorination (Cl_2) of (+)-**49** ($[\alpha]_D^{23}$ +33.2°, cyclohexane, Scheme 6) yields (+)-chlorosilane **68** ($[\alpha]_D^{23}$ −6.22°, cyclohexane) with retention and benzyllithium or benzylsodium then converts the (−)-**68** to (−)-**66** ($[\alpha]_D^{23}$ −6.68°, cyclohexane) by inversion.[17c] The overall stereochemistries of conversions of (+)-**49** to (−)-**66** in Schemes 6 and 9 and in Scheme 10 are thus identical and involve single inversions. Further, there is no significant difference in the stereochemistry of reactions of (+)-**23** with sodium methoxide at 25 °C and 0 °C and therefore, under the conditions studied, there is no evidence for pseudorotation during formation of (+)-**64** (Scheme 9). The exact stereospecificity in reaction of (+)-**23** with sodium methoxide resulting in

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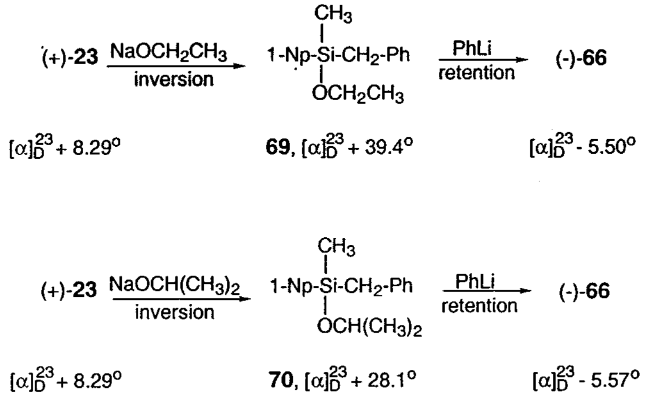
(23) The phenyl/1-naphthyl migratory aptitudes were determined by decomposing the **64** and **65** with excess TBAF/H_2O and determining by GLC the **21** and 1-methylnaphthalene formed.

(24) (a) Authentic methoxysilane (+,−)-**64** was prepared (see Experimental Section) by reaction of trimethoxymethylsilane and 1-naphthylmagnesium bromide and then displacement of the resulting dimethoxymethyl-1-naphthylsilane with benzylmagnesium chloride. (b) Methoxysilane (+,−)-**65** was synthesized (see Experimental Section) by coupling dimethoxymethylphenylsilane with 1-naphthylmethylmagnesium chloride.

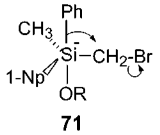
Scheme 11



migration of the 1-naphthyl group was not determined because (+)-**65** is formed in low yield, and the product could not be purified completely. It is clear, however, from the sign of its rotation that (+)-**65** (Scheme 9) is formed from (+)-**23** with overall inversion.

Rearrangement−displacements (Scheme 11) of (+)-**23** $[[\alpha]_D^{23}$ $-8.29°$, cyclohexane$]_l$ also occur with sodium ethoxide and with sodium 2-propoxide in dioxane at 23 °C. (+)-Benzylethoxysilane **69** ($[\alpha]_D^{23}$ + 39.4°, cyclohexane) and (+)-benzyl-2-propoxysilane **70** ($[\alpha]_D^{23}$ +28.1°, cyclohexane), respectively, are formed by phenyl migrations. 1-Naphthyl migrations in these experiments are very small. The gross structures of (+)-**69** and (+)-**70** are assigned upon direct comparison with racemic **69** and **70**, respectively, prepared by reactions of (+,−)-**64** with ethanol and 2-propanol at 80 °C in toluene containing potassium hydroxide. Displacements of the (+)-**69** and the (+)-**70** with phenyllithium (Scheme 11) in Et_2O then occur with retention[16a,17c] to give (−)-**66** of $[\alpha]_D^{23}$ −5.50° and −5.57°, respectively, in cyclohexane. Rearrangement−displacements of (+)-**23** by sodium ethoxide and sodium 2-propoxide to give (+)-**69** and (+)-**70**, respectively, are thus concluded to occur with (at least) 95% inversion at silicon, and pseudorotation is insignificant in these reactions.

The inversions in the rearrangement−displacements of (+)-**23** by alkoxides to give (+)-**64**, (+)-**69**, and (+)-**70** are understandable on the basis of nucleophilic attack on silicon from a direction opposite the phenyl group via pyramidal (pentacoordinate) intermediates and/or transition states as pictured in **71**. Expulsion of bromide ion with migration of the phenyl group to C-1 therefore results in inversion of the configuration about silicon and corresponds to traditional Walden inversions in bimolecular rearrangement−displacements reactions of varied carbon compounds. Though probably less likely to occur, hexacoordinate processes such as in **72** will also result in inversion about silicon.



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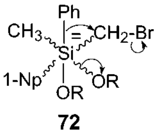

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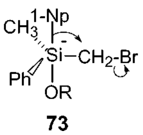

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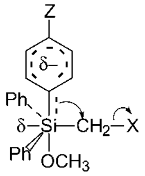
Of note is that phenyl migrates much more readily (∼10.5:1) than 1-naphthyl in reactions of (+)-**23** with alkoxides. This fact implies that there are important steric and conformational effects in formation and decomposition in pentacoordinate silylanionic processes possibly as in **71** (and/or **72**) and **73** or otherwise. In trigonal bipyramidal processes **71** can be favored over **73** because the constraints during formation or (and) rearrangement−displacements will be less when the smaller, more mobile phenyl group is in an apical position and the relatively bulky 1-naphthyl group is basal. Of particular interest is that the stereochemistries of rearrangement−displacements of (+)-**23** with alkoxides as in **71** are also consistent with behavior expected for pyramidal transition states **74** and **75** in reactions of **14a**−**f** with sodium methoxide in that electron-withdrawing substituents increase the migratory aptitudes of phenyl groups and the *ρ* value in the linear free energy correlation as in Figure 1f is small and positive. It is presently clear that the mechanistic details of rearrangement−displacements of (halomethyl)silanes by alkoxides are considerably simpler and better understood than with fluorides.



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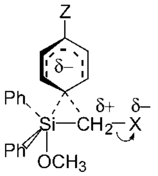

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Studies of synthesis and nucleophilic rearrangement−displacements of 2-halo-1-methyl-1-phenylsilacycloalkanes of fixed stereochemistries have been initiated.

Summary

In reactions of **13** (X = Cl) and F⁻ in THF at 25 °C, electron-withdrawing substituents increase the migratory aptitudes of the phenyl groups and correlations of logarithms of the migratory aptitudes with *σ* and with *σ*-zero substituent values are linear. Such correlations for F⁻ with **13** (X = Cl) at lower temperatures and **14** (X = Br) and **15** (X = I) at various temperatures, however, are unsatisfactory. Electron-donor groups have little effect or even accelerate aryl migrations in these latter systems. Rearrangement−displacements of (+)-**23** with F⁻ yield optically inactive **51**; the migratory aptitudes of the phenyl group are much greater (∼10.5:1) than for 1-naphthyl. For **14** (X = Br) and sodium methoxide in dioxane at 0 °C, electron-withdrawing substituents accelerate migration of the varied phenyl groups and the migratory aptitudes correlate well. Further, reactions of (+)-**23** with sodium methoxide, sodium ethoxide, and sodium 2-propoxide in dioxane involving phenyl migrations yield (+)-**64**, (+)-**69**, and (+)-**70**, respectively, with >93−95% inversion about silicon. 1-Naphthyl migrations in rearrangement−displacements of (+)-**23** with sodium methoxide to give (+)-**65** also occur with inversion. The migratory aptitudes of the phenyl and the 1-naphthyl groups in reactions of (+)-**23** and sodium methoxide are ∼9:1. Rearrangement−displacements in distorted trigonal bipyramidal (pentacoordinate) silicanionic intermediates such as **71** (and/or closely related transition states) in which the entering nucleophile is apical to silicon and backside to the migrating aryl group in the remaining apical position will give the inversions found for (+)-**23** with alkoxides. Pseudorotation in reactions of (+)-**23** with alkoxides is not evident. In rearrangement−displacements of **14** (X = Br) by sodium methoxide, phenyl groups which are relatively electron-deficient presumably occupy apical positions preferentially and migrate nucleophilically with displacement of Br^-. Further, the facts that the migratory aptitudes of the phenyl group are much larger than for 1-naphthyl in reactions of (+)-**23** with F^- and CH_3O^- indicate that primarily because of steric effects in the rearrangement−displacement acts the phenyl group is preferentially apical and attack on C-1 is less hindered than for such behavior of the 1-naphthyl group.

Experimental Section

General Information. Reactions were conducted in oven-dried glassware under dry argon. Migratory aptitude experiments were conducted in sealed sample vials. Gas chromatographic yields were determined using internal standards and peak areas were corrected for response factors of the flame ionization detector. The GC capillary column consisted of a 15 m × 0.53 mm bonded FSOT and a polyphenylmethylsiloxane 1.2 μm stationary phase. ^1H NMR spectra (250 MHz) were obtained in $DCCl_3$. Proton NMR peaks are reported in parts per million using $HCCl_3$ resonance at 7.26 ppm as the standard. Melting points were obtained on a capillary melting point unit and are uncorrected. MS values are based on ^{35}Cl, ^{79}Br, and ^{29}Si. Optical rotations were determined in a 1 dm cell using Na/cont light (589 nm) at 23 °C. Carbon and hydrogen combustion analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Chloro(chloromethyl)diphenylsilane (26) and (Chloromethyl)triphenylsilane (13c). Phenylmagnesium bromide (25, freshly prepared, 250 mL of a 2.35 M solution in Et_2O, 0.588 mol) was added dropwise to trichloro(chloromethyl)silane[7c] (24, 54.1 g, 0.294 mol) in anhydrous Et_2O (100 mL) at room temperature. The mixture was refluxed 5 h and then filtered through Celite. The magnesium salts were rinsed with anhydrous Et_2O. Concentration in vacuo followed by rapid distillation from the remaining magnesium salts gave a liquid (bp 96−155 °C/3 Torr) which was redistilled through a stainless steel column to yield **26** (53.3 g, 0.199 mol, 68%) as a clear liquid: bp 136−140 °C/2.5 Torr [lit.[7b] 187−192 °C/10 Torr]; ^1H NMR ($CDCl_3$) δ 7.80−7.25 (m, 10H), 3.40 (s, 2H); exact mass calcd for $C_{13}H_{12}Cl_2Si$ m/e 266.006; found 266.0164.

Addition of absolute ethanol (30 mL) to the pot residue from distillation of **26** led to crystallization of an off-white solid. Recrystallization from petroleum ether gave **13c** (3.2 g, 10 mmol, 4%) as white plates: mp 113−116 °C, lit.[7a] 112−115 °C; ^1H NMR ($CDCl_3$) 7.65−7.25 (m, 15H), 3.45 (s, 2H); exact mass calcd for $C_{19}H_{17}ClSi$ m/e 308.0789, found 308.0745.

(Chloromethyl)diphenyl(*p*-trifluoromethylphenyl)silane (13a), Procedure A. A solution of n-BuLi (15 mmol) in hexanes (15 mmol) was added (~30 min) to bromo(*p*-trifluoromethyl)benzene (0.33 g, 15 mmol) in Et_2O (20 mL) at −40 °C. The mixture was allowed to warm gradually to ~15 °C until testing[25a] revealed that all of the n-BuLi had reacted.

The (*p*-trifluoromethyl)phenyllithium solution was added to **26** (3.5 g, 13 mmol) in Et_2O (10 mL) at −40 °C. The mixture was allowed to warm to room temperature (~1 h) until the lithium reagent had completed its reactions. Water (30 mL) was added. The mixture was separated and extracted twice with Et_2O. The Et_2O solutions were combined, washed with H_2O and saturated aqueous NaCl, and dried over anhydrous $MgSO_4$. After filtration and concentration in vacuo, a white solid was obtained. Recrystallizations from Et_2O and from hexane gave **13a**: white needles (51%); mp 98−100 °C; ^1H NMR ($CDCl_3$) δ 7.65−7.20 (m, 14H), 3.45 (s, 2H); exact mass calcd for $C_{19}H_{14}F_3Si$ [$M^+ - (CH_2Cl)$] m/e 327.0817, found 327.0802. Anal. Calcd for $C_{20}H_{16}ClF_3Si$: C, 63.74; H, 4.25. Found: C, 64.00; H, 4.29.

Reactions of **26** as in Procedure A with *p*-chlorophenyllithium and *p*-methoxyphenyllithium were used for preparation (see Supporting Information) of chloromethyl(*p*-chlorophenyl)diphenylsilane (**13b**, 54%) and chloromethyl(*p*-methoxyphenyl)diphenylsilane (**13e**, 30%), respectively.

(Chloromethyl)[4-dimethylamino)phenyl]diphenylsilane (13f). Procedure B. To a suspension of freshly cut lithium chips (0.23 g, 33 mmol) in Et_2O (5 mL) was added bromo(4-dimethylamino)benzene (0.30 g, 15 mmol) in Et_2O (20 mL) at a rate (~30 min) to cause reflux. The reaction mixture was refluxed 2 h and then added to a stirred solution of **26** (3.5 g, 13 mmol) in Et_2O (10 mL) at room temperature. The mixture was refluxed until the Gilman test[25a] for organolithium reagents was negative (~1 h). After addition of H_2O, the ethereal solution was dried, concentrated, and cooled. The slightly yellow solid which separated was recrystallized from methylene chloride at −78 °C and then from hexane to give white needles of **13f**: yield (30%); mp 106−110 °C; ^1H NMR ($CDCl_3$) δ 7.55−6.55 (m, 14H), 3.40 (s, 2H), 2.95 (s, 6H); exact mass calcd for $C_{21}H_{22}ClNSi$ m/e 351.1213, found 351.1163. Anal. Calcd for $C_{21}H_{22}ClNSi$: C, 71.69; H, 6.26. Found: C, 71.49; H, 6.23.

(Chloromethyl)(*p*-methylphenyl)diphenylsilane (**13d**, see Supporting Information) was prepared (54%) from **27** (Z-*p* = CH_3) and **26** as in Procedure B.

(Dibromomethyl)diphenyl(*p*-trifluoromethylphenyl)silane (29a), Procedures C and D. n-BuLi (8.9 mL, 2 M in hexane, 0.022 mol) was added in Procedure C in 15 min to *p*-bromobenzotrifluoride (5.0 g, 0.022 mol) in dry Et_2O (25 mL) under argon at −40 °C. The solution was stirred 10 min, warmed to room temperature, added dropwise to dichlorodiphenylsilane (6.3 g, 0.025 mol) in Et_2O (20 mL), and refluxed 8 h. The Et_2O was removed by distillation while adding benzene (100 mL) until the stillhead temperature reached 78 °C. The mixture was filtered and concentrated at reduced pressure to give (chloro)diphenyl(*p*-trifluoromethylphenyl)silane, an orange oil (11.0 g), that was dissolved in Et_2O (40 mL) and added at 0 °C to $LiAlH_4$ (0.60 g, 0.016 mol) in Et_2O (20 mL). The solution was refluxed overnight, quenched at 0 °C with Et_2O saturated with H_2O, and treated with 10% acetic acid (45 mL). The organic layer was separated, washed with 10% acetic acid (50 mL), H_2O, and brine, dried over sodium sulfate, filtered, and fractionally distilled to yield diphenyl(*p*-trifluoromethylphenyl)silane (**28a**, 5.1 g, 0.016 mol, 70%): bp 145−150 °C/0.05 Torr; ^1H NMR ($CDCl_3$) δ 7.7−7.3 (m, 14H), 5.50 (s, 1H).

A stirred solution of **28a** (4.93 g, 0.015 mol) and phenyl(tribromomethyl)mercury (7.94 g, 0.015 m) in benzene (75 mL) in Procedure D was heated at 85 °C for 4 h. The mixture was filtered, concentrated at reduced pressure, dissolved in pentane, filtered, evaporated, and then chromatographed on silica gel using 90% hexane/10% benzene as the eluent. Isolation and crystallization of the product from hexane yielded **29a** (3.1 g, 0.0062 mol, 41%): white crystals; mp 108−109.5 °C; ^1H NMR ($CDCl_3$) δ 7.86−7.40 (m, 14H), 5.76 (s, 1H); MS (no M^+ was observed) 327.0832 ($C_{19}H_{14}F_3Si$, 100%). Anal. Calcd for $C_{20}H_{15}Br_2F_3Si$: C, 48.02%; H, 3.02%. Found: 47.92%, H, 3.05%.

(*p*-Chlorophenyl)(dibromomethyl)diphenylsilane (**29b**, 42%), (dibromomethyl)triphenylsilane (**29c**, 30%), (dibromomethyl)(*p*-methylphenyl)diphenylsilane (**29d**, 53%), and (dibromomethyl)(*p*-methoxyphenyl)diphenylsilane (**29e**, 58%) were prepared from (*p*-chlorophenyl)diphenylsilane (**28b**), triphenylsilane (**28c**), (*p*-methylphenyl)diphenylsilane (**28d**), and (*p*-methoxyphenyl)diphenylsilane (**28e**), respectively, upon extension of Procedure D.

(Bromomethyl)diphenyl(*p*-trifluoromethylphenyl)silane (14a), Procedure E. n-BuLi (1.05 mL, 2.5 M, 2.6 mmol) in hexane was added in 5 min to **29a** (1.25 g, 2.5 mmol) in Et_2O (48 mL) at −78 °C under argon. The solution was stirred 10 min at −78 °C and then treated with gaseous HBr for 10 s. The mixture was warmed to room temperature, and H_2O was added. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Chromatography of the residue on silica gel using 90% hexane/10% benzene as eluent, solution of the product in pentane, and

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(25) (a) Gilman, H.; Schulze, F. *J. Am. Chem. Soc.* **1925**, *47*, 2002. (b) Gilman, H.; Swiss, J. *J. Am. Chem. Soc.* **1940**, *62*, 1847.

crystallization at −10 °C yielded **14a** (0.60 g, 1.4 mmol, 56%): white crystals; mp 73−74 °C; ^{1}H NMR ($CDCl_3$) δ 7.74−7.38 (m, 14H), 3.20 (s, 2H); MS M$^+$ 420.1286 ($C_{20}H_{16}BrF_3Si$, 0.38%), 327.0878 ($C_{19}H_{14}F_3Si$, 100%). Anal. Calcd for $C_{20}H_{16}BrF_3Si$: C, 57.01%, H, 3.83%. Found. C, 57.10%; H, 3.87%.

(Bromomethyl)(*p*-chlorophenyl)diphenylsilane (**14b**, 67%), (bromomethyl)triphenylsilane (**14c**, 44%), (bromomethyl)(*p*-methylphenyl)diphenylsilane (**14d**, 45%), and (bromomethyl)-(*p*-methoxyphenyl)diphenylsilane (**14e**, 39%) were prepared by reactions of **29b**−**e**, respectively, with n-BuLi and then HBr as in Procedure E for **14a**.

(Bromomethyl)(*p*-dimethylaminophenyl)diphenylsilane (14f). Bromo(*p*-dimethylamino)benzene (1.96 g, 9.8 mmol) in THF (10 mL) was added in 30 min to magnesium (0.25 g, 10 mmol) in THF (10 mL) at room temperature. After being stirred for 2 h, the mixture was added to (bromomethyl)-chlorodiphenylsilane (3.05 g, 9.8 mmol) in THF (15 mL). The resulting solution was stirred for 8 h, concentrated at reduced pressure, and taken up in Et_2O/H_2O. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and vacuum-concentrated. The oily residue was chromatographed on silica gel (150 g) using 98% hexane/2% ethyl acetate as eluent. Isolation and crystallization of the product from hexane gave **14f** (1.62 g, 0.004 mol, 41%): white crystals; mp 105−107 °C; ^{1}H NMR ($CDCl_3$) δ 7.62−7.33 (m, 12H), 6.75−6.72 (d, 2H), 3.16 (s, 2H), 2.99 (s, 6H); MS M$^+$ 395.0722 ($C_{21}H_{22}BrNSi$, 10.36%), 302.1412 ($C_{20}H_{20}NSi$, 100%). Anal. Calcd for $C_{21}H_{22}NSi$: C, 63.63%, H, 5.59%. Found. C, 63.48%; H, 5.64%.

(Iodomethyl)diphenyl(*p*-trifluoromethylphenyl)silane (15a), Procedure F. A solution of **13a** (0.90 g, 2.4 mmol) and sodium iodide (1.44 g, 0.96 mmol) in anhydrous acetonitrile (20 mL) was heated at 82 °C for 48 h. The mixture was cooled to room temperature, diluted with Et_2O, filtered, and concentrated at reduced pressure. The residue was dissolved in hexane, filtered, and evaporated to an oil that was chromatographed on silica gel using 90% hexane/10% benzene as eluent. Isolation after recrystallization from hexane yielded **15a** (0.73 g, 1.56 mmol, 65%): white crystals; mp 67−68.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.74−7.37 (m, 14H), 2.72 (s, 2H); MS M$^+$ 467.9978 ($C_{20}H_{16}F_3ISi$, 2.87%), 327.0822 ($C_{19}H_{14}F_3Si$, 100%). Anal. Calcd for $C_{20}H_{16}F_3ISi$: C, 51.29%; H, 3.44%. Found: C, 51.34%; H, 3.45%.

(*p*-Chlorophenyl)(iodomethyl)diphenylsilane (**15b**, 29%), (iodomethyl)triphenylsilane (**15c**, 60%), (iodomethyl)(*p*-methylphenyl)diphenylsilane (**15d**, 49%), iodomethyl(*p*-methoxyphenyl)diphenylmethane (**15e**, 39%) and (*p*-dimethylaminophenyl)(iodomethyl)diphenylsilane (**15f**, 55%) were prepared from **13b**−**e** and **14f**, respectively, by reactions with KI upon extension of Procedure E.

Migratory Aptitudes from Reactions of 13a−f, 14a−f, and 15a−f, with TBAF. General Method: The halosilane (**13a**−**f**, **14a**−**f**, and **15a**−**f**, 0.15−0.22 mmol) in THF (0.3 mL) was added in 2 min to a 1.0 M solution of TBAF (0.35 mL, 0.35 mmol). The mixture was stirred until TLC revealed that reaction of the halosilane was complete (25 °C, ∼8 h; 0 °C, 10−15 days; −20 °C 18−24 days). Water (2.0−2.5 mL) and then pentane (0.2−0.3 mL) were added. The mixture was separated and extracted with pentane (4 × 0.30 mL). Anisole, an internal standard, was added at the beginning of an experiment or during workup of the products. The pentane fractions were combined and analyzed.

The amounts of **18** and **21** produced in each experiment were determined chromatographically. The migratory aptitudes were calculated from the **18** and **21** formed in each experiment and incorporate statistics in that each initial (halomethyl)silane (**13**−**15**) contains two phenyl groups and one *para*-substituted-phenyl group. The GC analysis for an individual toluene (**18** and **21**) is accurate to ∼± 5%,[10a] and thus the minimum error in the determinations of the migratory aptitudes in each experiment is ∼± 10%.[10a−c] The reactions for almost every (halomethyl)silane (**13**−**15**) with TBAF at a single temperature were conducted from 3 to 11 times, and the total yields of **18** and **21** in all experiments ranged from 93 to 106%. The mean and the standard deviation were calculated for the migratory aptitude of each substituted-phenyl group.[10b,c] The standard deviations in the migratory aptitudes for the *p*-methoxyphenyl and the *p*-dimethylaminophenyl groups in reactions of **13e** and **13f** are slightly larger than the minimum errors (±10%) because the GC peak areas for the substituted-toluenes (**18e** and **18f**) are small and broad compared to **21** and the standard.[10b,c] The errors in the migratory aptitudes for these substituted-phenyl groups are assumed to be the standard deviations of their mean migratory aptitudes.[10b,c] The mean values for the migratory aptitudes for all of the other substituted-phenyl groups in reactions of **13** and fluoride ion have standard deviations smaller than the minimum error (±10%) and thus the errors are assumed to be ±10%.[10b,c] The average relative error for all the migratory aptitudes is only ±13%.[10b,c]

Reactions of 14f with TBAF in 96% Hexane−4% THF and in Dioxane. Silane **14f** (0.0517 g, 0.1304 mol) was added to a mixture prepared from TBAF in THF (0.160 mL, 2.44 μL) and hexane (4 mL). The TBAF was quite insoluble in the reaction mixture. The solution was stirred for 2 weeks at ∼25 °C, and anisole (0.0134 g) was added. Gas chromatographic analysis of the reaction mixture revealed the presence of (1) **21** (0.0655 mmol, 50%), (2) anisole (standard), and (3) **18**, Z-*p* = $N(CH_3)_2$ (0.0543 mmol, 42%).

In a similar experiment a solution of **14f** (0.0581 g, 0.147 mmol) and anisole (0.0135 g) in dioxane (0.2 mL) was added in 2 min to TBAF (1 M, 0.34 mL, 0.34 mmol) in dioxane at 23 °C. The solution was stirred 18 h and worked-up as in the General Method. The analytical results are (1) **21** (0.0886 mmol, 60%), (2) anisole (standard), and (3) **18**, Z-*p* = $N(CH_3)_2$ (0.0539 mmol, 37%).

Reaction of (+)-23 with CsF. A mixture of (+)-**23** (0.112 g, 0.328 mmol; $[\alpha]_D^{23}$ + 8.29°, cyclohexane)[6] and CsF (0.228 g, 1.50 mmol) in dry THF (4 mL) was stirred overnight at room temperature, diluted with hexane, filtered, and concentrated at reduced pressure. The residue, on chromatography on silica gel using 75% hexane/25% benzene as eluent, yielded fluorosilane (+,−)-**51** (0.034 g, 0.1213 mmol, 37%; $[\alpha]_D^{25}$ + 0.00°, cyclohexane); ^{1}H NMR ($CDCl_3$) δ 8.05−7.00 (m, 12H), 2.74−2.55 (octet, 2H), 0.60−0.57 (d, 3H); MS M$^+$ 280.1051 ($C_{18}H_{17}FSi$, 36.8%), 189.0596 ($C_{11}H_{10}FSi$, 100%). The product is essentially identical with (+,−)-**51** prepared from (+,−)-**54** and BF_3 etherate as described later.

Rearrangement−Displacement of (+)-23 with CsF. Reaction of 51 with Phenyllithium. Reaction of (+)-**23** (0.1122 g, 0.3287 mmol; $[\alpha]_D^{23}$ +8.29°, hexane)[16b] and CsF (0.220 g, 0.00151 mol) was effected as in the previous experiment. After concentration at reduced pressure, the residue (**51**) was dissolved in Et_2O (4 mL), treated with 1.8 M phenyllithium (0.54 mmol), stirred overnight, concentrated, and filtered. Chromatography on silica gel (90% hexane/10% benzene as eluent) gave (+,−)-**53** (0.031 g, 0.0916 mmol, 28%; $[\alpha]_D^{25}$ + 0.00°, cyclohexane), an optically inactive product identical with authentic (+,−)-**53**.

Reaction of (+)-23 with TBAF. Silane (+)-**23** (0.126 g, 0.369 mmol, $[\alpha]_D^{23}$ + 8.29°, cyclohexane) in THF (2 mL) was treated with TBAF solution (1 M, 0.40 mL, 0.40 mmol) in THF (5 mL) for 10 s at room temperature and immediately diluted with pentane (100 mL) cooled to −78 °C. The solution was filtered, and the cold solvent was removed quickly at reduced pressure. The residue was chromatographed rapidly on silica gel using 75% hexane/25% hexane as eluent to give a mixture (0.0511 g) of **51** and **23** which in cyclohexane (1 mL) had an observed optical rotation of $\alpha_D^{25} = 0.110°$. ^{1}H NMR integration of the mixture in cyclohexane revealed **23** and **51** to be present in a ratio of 1:4. From the 1H NMR analysis the optical rotation of the mixture was calculated to be due to initial (+)-**23**.

Synthesis of (+,−)-Benzylfluoromethyl-1-naphthylsilane (51). A mixture of (+,−)-**54** (0.75 g, 2.56 mmol) and BF_3 etherate (0.5 mL) in Et_2O (10 mL) was stirred 4 h and concentrated under vacuum. Recrystallization of the residue from hexane gave (+,−)-**51** (0.26 g, 0.928 mmol, 36%): white crystals; mp 70.5−73 °C; ^{1}H NMR ($CDCl_3$) δ 8.04−7.00 (m, 12H), 2.73−2.54 (octet, 2H), 0.60−0.57 (d, 3H); MS M$^+$

280.1079 ($C_{18}H_{17}FSi$, 31.77%), 189.0593 ($C_{11}H_{10}FSi$, 100%). Anal. Calcd for $C_{18}H_{17}FSi$: C, 77.10%; H, 6.11%. Found: C, 77.03%; H, 6.15%.

Migratory Aptitudes in Reactions of (+)-23 with TBAF. To (+)-**23** (0.0547 g, 0.1603 mol) in THF (0.20 mL) was added 1 M TBAF (0.40 mL, 0.4 mmol) in THF. The mixture was stirred overnight, worked-up upon addition of H_2O (2 mL), and extracted with pentane (4 × 0.4 mL). Anisole was added as an internal standard to the combined extract. The solution was analyzed by GC methods. The analysis revealed (1) **21** (0.1333 mol, 83%), (2) anisole (standard), and (3) 1-methylnaphthalene (0.012 mol, 8%). The mole ratio of **21** to 1-methylnaphthalene and thus the migratory ratio of the phenyl and the 1-naphthyl groups from reactions of (+)-**23** with F^- is 10.4:1. Benzene and naphthalene are also produced in cleavage of **52** and **51** by F^- and protonation. The ratio of benzene to naphthalene was not quantified.

Racemization of (−)-Fluoromethyl-1-naphthylphenylsilane (58) by TBAF in THF. Experiment 1: a solution of **58** (0.0147 g, 6.17×10^{-2} mmol) in THF (1 mL) in an optical cell at room temperature had a rotation (α) of −0.631° (α_D). To the cell was added 0.01 mL of 1 M TBAF in THF. The cell was immediately placed in a polarimeter and in ~10 s gave a rotation (α) of −0.556° (α_D). The rotations (α) of the partially heterogeneous solution as monitored every 5 s during the next 80 s dropped progressively from −0.544° (α_D) to −0.412° (α_D). Upon then stirring the cell contents quickly, the mixture became completely homogeneous and gave an immediate rotation of α = 0.00° (α_D). Experiment 2: a solution of (−)-**58** (0.0236 g, 9.9×10^{-2} mmol) in THF (1 mL) at room temperature had a rotation of α = −0.734° (α_D). The solution, after addition of 1 M TBAF (0.01 mL), rapid stirring, and immediate measurement, was optically inactive (α = 0.00° (α_D)).

Dimethoxyphenyl(phenylmethyl)silane (63). Benzyl chloride (40.0 mL, 44.0 g, 0.348 mol) in Et_2O (50 mL) was added to a stirred suspension of magnesium turnings (10.0 g, 0.411 mol) in Et_2O (150 mL), and the mixture was refluxed 2 h. An aliquot of the benzylmagnesium chloride solution (175 mL, 1.42 M; 0.248 mol) was added (~2 h) to trimethoxyphenylsilane[27] (49.0 g, 0.247 mol) in Et_2O (100 mL) under argon. The mixture was refluxed until the test for the Grignard reagent[25a] was negative (~5 h) and then cooled. Hydrochloric acid (10%) and water were added. The aqueous layer was separated and extracted with Et_2O. The combined Et_2O extracts were washed with H_2O and saturated aqueous NaCl, dried over $MgSO_4$, filtered, concentrated in vacuo, and distilled through a glass column packed with stainless steel staples to yield **63**, a clear colorless liquid (34.6 g, 0.134 mol, 54%): bp 105−120 °C/0.4 Torr; ^{1}H NMR δ 7.50−6.90 (m, 10H), 3.50 (s, 6H), 2.30 (s, 2H); exact mass calcd for $C_{15}H_{18}O_2Si$ *m/e* 258.1076, found 258.1082. Anal. Calcd for $C_{15}H_{18}O_2Si$: C, 69.77; H, 6.98. Found: C, 69.98; H, 6.89.

Migratory Aptitudes for Reactions of 14a−f with Sodium Methoxide. General Method. The migratory aptitudes in reactions of bromosilanes **14a−f** with sodium methoxide were determined as follows. The bromosilane (**14a−f**, 0.15 mmol) was added to sodium methoxide (generally 0.11 g, 2.0 mmol) in purified dioxane (0.40 mL). The resulting mixture was vigorously stirred at ~25 °C until TLC indicated no **14a−f** remained. The mixture was then treated with TBAF (2.3 equiv, 1 M in THF) and stirred at 25 °C for 8 h. [The excess fluoride ion assured cleavage of **17b** (Nuc = CH_3O) and **20b** (Nuc = CH_3O); fluoride attacks silicon in **17b** and **20b** much more rapidly than does methoxide]. The mixture was worked-up by addition of H_2O and extraction with pentane (4 × 0.3 mL). A known amount of the internal standard, anisole, was added to the combined pentane extracts, and the solution was analyzed by capillary GC as described previously. Similar experiments were executed using CsF in THF.

Reactions of (+)-23 with Sodium Methoxide. Bromosilane (+)-**23** [0.90 g, 2.64 mmol, $[\alpha]_D^{23}$ + 8.29° (0.0135 g in 1 mL of cyclohexane), lit [$[\alpha]_D^{23}$ + 9.15°][16d] was added to sodium methoxide (0.25 g, 0.046 mol) in dry dioxane (16 mL) under argon at room temperature. The solution was stirred 2 h while the reactions were followed by TLC. The mixture was diluted with hexane, filtered, concentrated, and chromatographed on silica gel. The eluent, 85% hexane/15% benzene, led to recovery of (+)-**23** [0.039 g, 1.04 mol, 43% recovery, $[\alpha]_D^{23}$ +8.21° (0.0195 g in 1 mL of cyclohexane)]. Use of the eluent, 97% hexane/3% ethyl acetate, allowed isolation of (+)-**64** and (+)-**65** in a 10.5:1 ratio (by ^{1}H NMR). Further chromatography of (+)-**23** and (+)-**64** on silica gel resulted in separation of (+)-**23** [0.112 g, 0.397 mol, 15%; $[\alpha]_D^{23}$ +39.5° (0.112 g in 5 mL of cyclohexane)]: ^{1}H NMR ($CDCl_3/CHCl_3$) δ 8.29−6.95 (m, 12H), 3.45 (s, 3H), 2.66−2.51 (q, 2H), 0.47 (s, 3H); MS M^+ 292.1257 ($C_{19}H_{20}OSi$, 8.69%), 201.0741 ($C_{12}H_{13}OSi$, 100%). The chromatographic and ^{1}H NMR properties of (+)-**64** are identical with those of (+,−)-**64** prepared as follows.

Synthesis of Racemic Benzylmethoxymethyl-1-naphthylsilane [(+,−)-64].[24] Benzylmagnesium chloride, prepared from benzyl chloride (1.28 g, 0.055 mol) and magnesium (1.28 g, 0.055 mol) in Et_2O (12 mL), was added to dimethoxymethyl-1-naphthylsilane[8a] (16.33 g, 0.07 mol) in dry Et_2O (25 mL). The mixture was refluxed 5 h, cooled, filtered, concentrated, and vacuum-distilled to give (+,−)-**64** (9.0 g, 0.031 mol, 62%) as an oil: bp 149−154 °C (0.05 Torr); ^{1}H NMR ($CDCl_3$) δ 8.36−7.00 (m, 12H), 3.49 (s, 3H), 2.71−2.55 (q, 4H), 0.52 (s, 3H); MS M^+ 292.1276 ($C_{19}H_{22}OSi$, 7.94%), 201.0756 ($C_{12}H_{13}OSi$, 100%). Anal. Calcd for $C_{19}H_{20}OSi$; 78.03%; H, 6.89%; Found C, 78.16; H, 6.90.

Synthesis of Racemic Methoxymethyl-(1-naphthylmethyl)phenylsilane [(+,−)-65]. 1-Naphthylmethylmagnesium chloride, prepared from 1-chloromethylnaphthalene (8.83 g, 0.05 mol), magnesium (1.28 g, 0.53 mol), Et_2O (22.5 mL), and benzene (25 mL), was added dropwise to dimethoxymethylphenylsilane (9.12 g, 0.05 mol) in Et_2O (25 mL). The mixture was heated at 55 °C for 3 h, cooled, filtered, and distilled to give (+,−)-**65**: bp 145−149 °C/0.05 Torr; ^{1}H NMR ($CDCl_3$) δ 8.01−7.21 (m, 12H), 3.44 (s, 3H), 3.03−2.83 (q, 2H), 0.29 (s, 3H); MS M^+ 292.1259 ($C_{19}H_{20}Osi$, 13.13%), 151.0605 ($C_8H_{11}OSi$, 100%). Anal. Calcd for $C_{19}H_{20}OSi$: C, 78.03%; H, 6.98%. Found: C, 78.04%; H, 6.93%.

Conversion of (+)-64 by Phenyllithium to (−)-Benzylmethyl-1-naphthylphenylsilane [(−)-66]. Phenyllithium (0.13 mL, 1.8 M in Et_2O/cyclohexane) was added to (+)-**64** (0.0580 g, 0.198 mmol; $[\alpha]_D^{23}$ +39.5°, cyclohexane) in Et_2O (4 mL). The mixture was stirred 2 h, diluted with hexane, filtered, and concentrated at reduced pressure. Chromatography of the residue on silica gel using 90% hexane/10% benzene as eluent yielded (−)-**66** [0.0606 g, 0.179 mmol, 90%; $[\alpha]_D^{23}$ −5.25° (0.0606 g in 1 mL of cyclohexane)]: ^{1}H NMR ($CDCl_3$) δ 7.93−6.80 (m, 17H), 2.90−2.77 (q, 2H), 0.58 (s, 3H); MS M^+ 338.1498 ($C_{24}H_{22}Si$, 6.23%), 247.0974 ($C_{17}H_{15}Si$, 100%).

By the above procedure (+,−)-**64** was converted to (+,−)-**66** (58%) whose IR, ^{1}H NMR, and MS are identical with that of (−)-**66** as prepared from (+)-**64**. Anal. Calcd for $C_{24}H_{22}Si$: C, 85.13%; H, 6.55%. Found: C, 85.17%; H, 6.55%.

Reaction of (+)-23 with Phenylmagnesium Bromide/Cuprous Iodide To Give (+)-66. Phenylmagnesium bromide (0.3245 g, 1.79 mmol) in THF (10 mL) was added to (+)-**23** (0.550 g, 1.60 mmol, $[\alpha]_D^{23}$ +8.29°, cyclohexane) in THF (4 mL) containing a small amount of cuprous iodide. The resulting mixture was refluxed 6 h and cooled, and the solvent was removed at reduced pressure. The remaining material was chromatographed on silica gel using 90% hexane/10% benzene as eluent to give (+)-**66** (0.4518 g, 1.33 mmol), $[\alpha]_D^{23}$ +6.15° (0.3497 g in 5 mL of cyclohexane): ^{1}H NMR ($CDCl_3$) δ 7.90−6.82 (m, 17H), 2.91−2.79 (q, 2H), 0.59 (s, 3H); MS M^+ 338.1492 ($C_{24}H_{22}Si$, 5.72%), 247.0993 ($C_{17}H_{15}Si$, 100%).

Migratory Aptitudes in Reactions of (+)-23 with Sodium Methoxide. Bromosilane (+)-**23** (0.0630 g, 0.185 mmol) and sodium methoxide (0.119 g, 2.20 mmol) were added to dioxane (0.40 mL). The mixture was stirred 48 h. TLC revealed

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that no (+)-**23** remained. A solution of 1 M TBAF (0.60 mL, 0.60 mmol) in THF was added, and the mixture was stored overnight. Anisole (0.0158 g) was added as an internal standard, and the mixture was worked-up by addition of H_2O and extraction with pentane (4 × 0.4 mL portions). GLC analysis revealed the presence of **21** (0.149 mmol, 81%), anisole (standard), and 1-methylnaphthalene (0.0157 mol, 9%). The mole ratio of **21** to 1-methylnaphthalene, and thus the migratory ratio of the phenyl and the 1-naphthyl groups from reaction of (+)-**23** with sodium methoxide is 9:1. [In reactions of (+)-**23** with sodium methoxide and then protonation, benzene and naphthalene are produced as very minor products].

Reaction of (+)-23 with Sodium Ethoxide to Yield (+)-Benzylethoxymethyl-1-naphthylsilane (69). Sodium (0.0608 g, 2.64 mmol) was added to anhydrous ethanol. After depletion of the sodium, the excess ethanol was removed under high vacuum. The residue was placed under argon and (+)-**23** (0.65 g, 1.90 mmol, $[\alpha]_D^{23}$ +8.29°, cyclohexane) in dry dioxane (10 mL) was added. The mixture was stirred 4 h at 23 °C, diluted with hexane, filtered, and concentrated at reduced pressure. The oily residue, on chromatography on silica gel with 90% hexane/10% benzene as eluent, yielded initial (+)-**23** (0.3182 g, 0.9323 mmol, 49%). Using 97% hexane/3% ethyl acetate as eluent gave (+)-**69** [(0.0571 g, 0.186 mmol, 19%, $[\alpha]_D^{23}$ 39.4° (0.0571 g in 3 mL of cyclohexane)]: ^{1}H NMR ($CDCl_3$, TMS 0.0817) δ 8.34−6.93 (m, 12H), 3.69−3.66 (q, 2H), 2.64−2.52 (q, 2H), 1.20−1.14 (t, 3H), 0.46 (s, 3H); MS M$^+$ 306.1434 ($C_{20}H_{22}OSi$, 14.38%), 215.0856 ($C_{13}H_{15}OSi$, 100%).

Conversion of (+,−)-64 by Sodium Ethoxide to (+,−)-69. To ethanol (3 mL) in toluene (20 mL) were added (+,−)-**64** (0.62 g, 2.10 mmol) and a small amount of KOH. The solution was heated at 80 °C for 4 h, cooled to room temperature, filtered, and concentrated. Chromatography of the remaining oil on silica gel (8% hexane/2% ethyl acetate as eluent) yielded (+,−)-**69** (0.30 g, 0.98 mmol, 46%): ^{1}H NMR ($CDCl_3$, TMS 0.0011) δ 8.35−6.93 (m, 12H), 3.70−3.67 (q, 2H), 2.66−2.51 (q, 2H), 1.21−1.15 (t, 3H), 0.47 (s, 3H); MS M$^+$ 306.1453 ($C_{20}H_{22}OSi$, 10.35%), 215.0908 ($C_{13}H_{15}OSi$, 100%). Anal. Calcd for $C_{20}H_{22}OSi$, 78.12%; H, 7.54%. Found: C, 78.31%; H, 7.29%.

Conversion of (+)-69 by Phenyllithium to (−)-66. Phenyllithium (0.11 mL, 1.8 M, 0.20 mmol) in Et_2O/cyclohexane was added to (+)-**69** (0.055 g, 0.18 mmol, $[\alpha]_D^{23}$ 39.4°, cyclohexane) in anhydrous Et_2O (5 mL). The mixture was stirred 6 h, concentrated at reduced pressure, and chromatographed on silica gel (90% hexane/10% benzene as eluent) to give (−)-**66** [(0.0521 g, 0.159 mmol, 85%), $[\alpha]_D^{23}$ −5.50° (0.040 g in 1 mL of cyclohexane)]: ^{1}H NMR ($CDCl_3$) δ 7.93−6.80 (m, 17H), 2.90−2.77 (q, 2H), 0.58 (s, 3H). The spectral properties of (−)-**66** are identical with previous samples.

Reaction of (+)-23 with Sodium 2-Propoxide To Give (+)-Benzylmethyl-1-naphthyl-2-propoxysilane 70. Sodium 2-propoxide was prepared from sodium (0.0645 g, 2.80 mmol) and 2-propanol (2 mL). After the excess 2-propanol had been removed at reduced pressure, the sodium 2-propoxide was placed under argon and (+)-**23** (0.65 g, 1.90 mmol, $[\alpha]_D^{23}$ +8.29°, cyclohexane) in dioxane (15 mL) was added. After being stirred 3 h at 23 °C, the mixture was diluted with hexane, filtered, and concentrated at reduced pressure. Chromatography of the remaining oil on silica gel with 90% hexane/10% benzene as eluent yielded (+)-**23** (0.36 g, 1.05 mmol, 55% recovery). Use of 98% hexane/2% ethyl acetate as eluent gave (+)-**70** [0.031 g, 0.0967 mmol, 11.4%; $[\alpha]_D^{23}$ 28.1° (0.031 g in 2 mL of cyclohexane)]: ^{1}H NMR ($CDCl_3$) δ 8.41−6.90 (m, 12H), 4.1−3.9 (septet, 1H), 2.64−2.51 (q, 2H), 1.17−1.10 (q, 6H), 0.49 (s, 3H).

Conversion of (+)-70 by Phenyllithium to (−)-66. Phenyllithium (0.06 mL, 1.8 M in Et_2O/cyclohexane, 0.108 mmol) was added to (+)-**70** (0.031 g, 0.0967 mmol, $[\alpha]_D^{23}$ +28.1°, cyclohexane) in Et_2O (5 mL). After 2 h, the solution was diluted with hexane, filtered, and concentrated at reduced pressure. The residue was chromatographed on silica gel using 90% hexane/10% benzene as eluent to yield (−)-**66** (0.0294 g, 0.0868 mmol, 90%; $[\alpha]_D^{23}$ −5.57°, 0.0294 g in 1 mL of cyclohexane): ^{1}H NMR ($CDCl_3$) δ 7.93−6.80 (m, 17H), 2.90−2.77 (s, 3H), 0.58 (s, 3H).

Conversion of (+,−)-64 by Sodium 2-Propoxide to (+,−)-70. 2-Propanol (6 mL) and KOH (a small amount) were added to (+,−)-**64** (0.62 g, 2.12 mmol) in toluene (25 mL). The stirred solution was heated to 80 °C for 2 days. Chromatography with 97% hexane/3% ethyl acetate yielded (+,−)-**70** (0.10 g, 0.31 mol, 15%): ^{1}H NMR ($CDCl_3$) δ 8.40−6.91 (12H), 4.08−4.00 (septet, 1H), 2.64−2.52 (q, 2H), 1.17−1.11 (q, 6H), 0.49 (s, 3H). The ^{1}H NMR of the (+,−)-**70** is essentially identical with that of (+)-**70** prepared previously.

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Supporting Information Available: Plots of the logarithms of the migratory aptitudes (*p*-Z-Ph/Ph) versus (1) σ-zero substituent values for reactions of **13a**−**f** with TBAF/THF at 0 °C and −20 °C, respectively, (2) σ substituent values for **13a**−**f** with TBAF/THF at −20 °C, and (3) σ-zero substituent values for **14a**−**f** with TBAF/THF at 0 °C and −20 °C, respectively, a table and discussion of the migratory aptitudes of the *p*-Cl-Ph- and the *p*-$(CH_3)_2$N-Ph- groups, respectively, in reactions of **14b** and **14f** in THF at 23 °C with TBAF at various concentrations, a summary and discussion of the optical behaviors of solutions of (+)-**23** with varied equivalents of TBAF at 23 °C, and procedures or directions for preparation of silanes **13b**,**d**,**e**, **14b**−**e**, **15b**−**f**, **17b** (Z-*p* = Cl), **17b** (Z-*p* = CH_3), **20b** (Z-*p* = Cl), **20b** (Z-*p* = H), **20b** (Z-*p* = CH_3), **28a**, **29b**−**e**, and **30**. This material is available free of charge via the Internet at http://pubs.acs.org.

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