Stereochemistry of Asymmetric Silicon. VIII. Stereochemistry Crossover and Leaving Group Basicity in Organometallic Coupling Reactions[1]

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Abstract: Coupling reactions of organolithium and Grignard reagents with optically active compounds, R_3Si^*-OMe and R_3Si^*H, are reported. These stereochemical results, plus those obtained previously with Cl and F leaving groups, show that stereochemistry crossover from *inversion* to *retention* of configuration is a sensitive function of the nature of the organometallic reagent and the basicity of the leaving group. The relationships that are revealed are consistent with earlier conclusions that *inversion* reactions of R_3Si^*X with strong nucleophiles proceed by mechanism S_N2–Si, and *retention* reactions by mechanism S_Ni–Si.

Extensive studies of the coupling reactions of optically active compounds containing the α-naphthylphenylmethylsilyl group, α-NpPhMeSi*, designated R_3Si^* below, with organolithium reagents have been reported previously for R_3Si^*Cl and R_3Si^*F.[2] These have shown that *inversion* of configuration is the stereochemical path followed by R_3Si^*Cl with *all types* of RLi reagents,[3] in accord with the S_N2–Si stereochemistry rule for good leaving groups.[4] For R_3Si^*F, however, simple alkyllithium and aryllithium reagents give *retention* of configuration, whereas allyllithium and benzyl-type lithium reagents give *inversion* of configuration. Thus, for R_3Si^*F stereochemistry of reaction is dependent upon the type of RLi reagent used.

In the present paper, our studies of the stereochemistry of organometallic coupling reactions at silicon centers have been extended to include systematic studies of the methoxide and hydride leaving groups. Both of these have been previously classified as poor leaving groups, on the basis that their conjugate acids, HX, have pK_a larger than 10,[5] and it has been proposed that for displacement of poor leaving groups from silicon, the predominant stereochemistry depends upon the relative importance of several factors and may be either *retention* or *inversion* of configuration in individual cases.[5]

Thus it was of interest to determine whether (like R_3Si^*F) R_3Si^*OMe and R_3Si^*H would exhibit variable stereochemistry dependent on the nature of RLi, and whether, if found, such variation would be consistent with the previous postulate of the retention reactions of RLi proceeding by a quasi-cyclic S_Ni–Si mechanism.[2,5]

Results obtained in 18 stereochemical studies are shown in Table I. For most of these, previous work has resulted in assignments of relative and absolute configuration to the R_3Si^*R' products[2] and such assignments permit present designation of predominant stereochemistry in such cases. However, the products obtained in reactions 3, 17, and 18 in Table I have not previously received configurational correlation and it was necessary to prepare them from R_3Si^*Cl on the assumption, based on the S_N2–Si stereochemistry rule, that R_3Si^*Cl and $R'Li$ react with inversion of configuration.

$$(-)\text{-}R_3Si^*Cl + o\text{-}CH_3C_6H_4Li \xrightarrow{\text{ether}} (-)\text{-}R_3Si^*C_6H_4\text{-}o\text{-}CH_3 \qquad (19)$$

$$(-)\text{-}R_3Si^*Cl + PhC{\equiv}CLi \xrightarrow{\text{ether}} (+)\text{-}R_3Si^*C{\equiv}CPh \qquad (20)$$

From reactions 19 and 20 it is clear that $(+)$-R_3Si^*-C_6H_4-o-CH_3 and $(-)$-$R_3Si^*C{\equiv}CPh$ have the same configuration as $(+)$-R_3Si^*H, $(+)$-R_3Si^*F, and $(+)$-R_3Si^*-OMe, and that the full names for these enantiomers are (R)-(+)-α-naphthyl-o-tolyphenylmethylsilane and (S)-(−)-α-naphthylphenylethynylphenylmethylsilane. In connection with the latter assignment of configuration, it is interesting to note from reactions 17 and 20 that $(+)$-R_3Si^*F and $(-)$-R_3Si^*Cl, which have the same configuration,[6] follow opposite stereochemical paths with PhC≡CLi. In this respect, PhC≡CLi behaves like simple alkyllithium and aryllithium reagents,[2] and the choice of *inversion* of configuration for reaction 20 of R_3Si^*Cl and *retention* of configuration for reaction 17 of R_3Si^*F is clearly the most reasonable one.

In connection with subsequent discussion, it is of interest to note the following additional stereochemical equations which deal with Grignard reagents and asymmetric silicon centers.

$$(+)\text{-}R_3Si^*OMe + C_2H_5MgBr \xrightarrow{Et_2O} (+)\text{-}R_3Si^*C_2H_5 \qquad (21)$$

$$(-)\text{-}R_3Si^*Cl + PhCH_2MgCl \xrightarrow{Et_2O} (+)\text{-}R_3Si^*CH_2Ph \qquad (22)$$

$$(+)\text{-}R_3Si^*F + PhCH_2MgCl \xrightarrow{Et_2O} (+)\text{-}R_3Si^*CH_2Ph \qquad (23)$$

$$(+)\text{-}R_3Si^*OMe + PhCH_2MgCl \xrightarrow{Et_2O} (+)\text{-}R_3Si^*CH_2Ph \qquad (24)$$

Reactions 21, 22, and 23 have been reported before, and 21 proceeds with *retention* of configuration,[2] 22 with *inversion* of configuration,[2,7] and 23 with *inversion* of configuration. It is of considerable significance that

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[1] For the preceding paper in this series, see L. H. Sommer and J. D. Citron, *J. Am. Chem. Soc.*, **89**, 5797 (1967).

[2] L. H. Sommer, W. D. Korte, and P. G. Rodewald, *ibid.*, **89**, 862 (1967).

[3] *Cf.* also A. G. Brook and C. M. Warner, *Tetrahedron Letters*, 815 (1962).

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

[5] L. H. Sommer, C. L. Frye, and G. A. Parker, *ibid.*, **86**, 3276 (1964); L. H. Sommer, *et al.*, *ibid.*, **83**, 2210 (1961).

[6] L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964).

[7] Reactions 22 and 23 in ref 2 have different sign relationships because the rotations of the benzylsilane products were reported in cyclohexane solvent. For $[\alpha]_D$ the signs of rotation are opposite in cyclohexane as compared to pentane solvent which is being referred to in eq 22 and 23 above. Stereochemistry assignments in ref 2 and in the present paper are the same.

Table I. Stereochemistry of Coupling Reactions of α-NpPhMeSi*X, R_3Si^*X, with Organolithium Reagents

Eq	R_3Si^*X reactant	Reagent[a]	Product	[α]D,[b] deg	Stereo-specificity, %[c,d]
1	(+)-SiOMe	C_2H_5Li	(+)-SiC_2H_5	+2.9	74 ret[e]
2	(+)-SiH	*n*-C_3H_7Li	(+)-SiC_3H_7	+1.7	100 ret[e]
3	(+)-SiOMe	*o*-$CH_3C_6H_4Li$	(+)-SiC_6H_4-*o*-CH_3	+21.7	97 ret[f]
4	(+)-SiOMe	$PhCH_2Li$	(+)-$SiCH_2Ph$	+3.9	79 inv[g]
5	(−)-SiO-(−)-Men	$PhCH_2Li$	(+)-$SiCH_2Ph$	+2.4	68 inv[g]
6	(+)-$SiOSi^*R_3$	$PhCH_2Li$	(+)-$SiCH_2Ph$	+2.8	70 inv[g]
7	(+)-SiH	$PhCH_2Li$	(−)-$SiCH_2Ph$	−5.5	90 ret[g]
8	(+)-SiOMe	$CH_2{=}CHCH_2Li$	(−)-$SiCH_2CH{=}CH_2$	−2.1	58 inv
9	(+)-SiH	$CH_2{=}CHCH_2Li$	(+)-$SiCH_2CH{=}CH_2$	+10.1	89 ret
10	(+)-SiOMe	(*p*-$CH_3OC_6H_4$)CH_2Li	(−)-$SiCH_2$(C_6H_4-*p*-OCH_3)	−11.3	90 ret
11	(+)-SiH	(*p*-$CH_3OC_6H_4$)CH_2Li	(−)-$SiCH_2$(C_6H_4-*p*-OCH_3)	−10.8	88 ret
12	(+)-SiOMe	$Ph(CH_3)CHLi$	(−)-$SiCH(CH_3)Ph$	−13.9	69 inv
13	(−)-SiO-(−)-Men	$Ph(CH_3)CHLi$	(−)-$SiCH(CH_3)Ph$	−25.2	85 inv
14	(+)-SiH	$Ph(CH_3)CHLi$	(+)-$SiCH(CH_3)Ph$	+26.5	87 ret
15	(+)-SiOMe	Ph_2CHLi	(+)-$SiCHPh_2$	+11.5[h]	82 inv[i]
16	(+)-SiH	Ph_2CHLi	(+)-$SiCHPh_2$	+3.7[h]	60 inv[i]
17	(+)-SiF	$PhC{\equiv}CLi$	(−)-$SiC{\equiv}CPh$	−7.6	92 ret
18	(+)-SiOMe	$PhC{\equiv}CLi$	(−)-$SiC{\equiv}CPh$	−9.1	100 ret

[a] Reactions were run in dry ether unless otherwise noted. [b] Rotations were taken on pentane solutions unless otherwise noted. For consistency of presentation, data are given for (+)-SiOMe, (+)-SiH, (−)-SiCl, (+)-$SiOSiR_3$, and (−)-SiO-(−)-Men, although sometimes their enantiomers were used. [c] A stereospecificity of, say, 90% means that the product was 80% optically pure (20% racemic), if an optically pure reactant was used. [d] In the case of the benzhydryl, benzyl, and *o*-tolyl derivatives, the products could be prepared optically pure by crystallization, thus indicating high stereospecificity for these reactions. In other cases, the product of highest rotation from reaction with a given R′Li was assumed to be optically pure (see ref 2). [e] Reaction carried out in pentane. [f] Based on the optically pure *o*-tolylsilane, [α]D +23.2°, obtained by recrystallization. [g] Based on the optically pure benzylsilane, [α]D +6.9° (pentane), obtained by recrystallization. [h] Chloroform solvent. [i] Based on the optically pure benzhydrylsilane, [α]D +17.7°, obtained by recrystallization.

Table II. Stereochemistry Crossover, Basicity of Leaving Group, X, and Nature of R′Li

Reaction series	Reagent	Stereochemistry of				Crossover	Crossover
		Cl	F	OMe	H	X[a]	pK_a[b]
I	Alkyllithium	inv	ret	ret	ret	F	∼4
II	Aryllithium	inv	ret	ret		F	∼4
III	$PhC{\equiv}CLi$	inv	ret	ret		F	∼4
IV	(*p*-$CH_3OC_6H_4$)CH_2Li	inv	inv	ret	ret	OMe	∼16
V	$PhCH_2Li$	inv	inv	inv	ret	H	∼40
VI	$Ph(CH_3)CHLi$	inv	inv	inv	ret	H	∼40
VII	$CH_2{=}CHCH_2Li$	inv	inv	inv	ret	H	∼40
VIII	Ph_2CHLi	inv	inv	inv	inv	None	

[a] For purposes of present and subsequent discussion, "crossover X" for a stereochemical reaction series is defined as: the *least* basic leav - inggroup giving *retention* of configuration. [b] "Crossover pK_a" for a stereochemical reaction series is defined as: pK_a of the conjugate acid (HX) of the crossover X.

reaction 24, in contrast to reaction 21, proceeds with predominant *inversion* of configuration, paralleling the change in stereochemistry of reaction of $R_3Si^*OCH_3$ with the change from C_2H_5Li to $PhCH_2Li$.

General Mechanism Considerations. Stereochemical data for a fairly broad spectrum of leaving groups and organometallic reagents is provided by the new results in the present paper and those previously reported for the chloride and fluoride groups.[2] This section will examine variation of stereochemistry with the basicity of the leaving group, X, and the nature of the organometallic reagent. Mechanism models are discussed in the next section.

The four leaving groups, X, to be discussed in some detail in connection with organometallic coupling reactions of R_3Si^*X are Cl, F, OMe, and H. Their basicities may be expressed in terms of the approximate pK_a values of the corresponding conjugate acids, HX. For pK_a of HX, reasonable approximate values are: Cl < -1; F, 4; OMe, 16; H, 40.[8] Clearly, the *order of decreasing basicity of X is H > OMe > F > Cl* and these four leaving groups cover a very wide range of basicity. Table II provides an over-all summary of the stereochemical data obtained for reactions of R_3Si^*X with R′Li.

Perhaps the most significant general aspect of the relationships between predominant stereochemistry of reaction, basicity of leaving group, and nature of R′Li can be discussed in terms of stereochemistry crossover. For eight stereochemical reaction series, Table II lists "*crossover X*," the *least* basic leaving group giving retention of configuration, and "*crossover pK*$_a$," the pK_a of the conjugate acid (HX) of the corresponding crossover X. From examination of these in the last two columns in Table II it is clear that *stereochemistry crossover is a sensitive function of the nature of R′Li.* Except for the Cl leaving group with conforms to the S_N2–Si stereochemistry rule of inversion of configuration for good leaving groups,[9] *predominant stereochemistry of F, OMe, and H depends on the nature of R′Li.*

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(8) Values of pK_a assigned to MeOH, CH_4, and C_2H_6 are 16, 40, and 42, respectively, in a recent excellent review. See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapter 1.

(9) Despite the fact that the pK_a of HF places F in the category of good leaving groups, the high bond energy of Si–F (∼150 kcal/mole), the small size of F, and the capacity of F for coordination with the electrophilic center of an attacking reagent frequently cause R_3Si^*F to react with retention of configuration by an S_Ni–Si mechanism.[2,4]

With respect to crossover X and crossover pK_a, the data of Table II fall into four groups. If we first choose to consider only reaction series I, IV, V, and VIII from these four groups, it is clear that increased charge delocalization in the carbanion corresponding to R'Li leads to increased basicity of crossover X, and to increased crossover pK_a values. In short, increased charge delocalization in R'^- favors an inversion stereochemistry for poor leaving groups of high basicity. Schematically

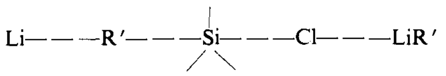
$$\underset{\text{reaction series changes}}{\mathrm{I} \longrightarrow \mathrm{IV} \longrightarrow \mathrm{V} \longrightarrow \mathrm{VIII}} \;\text{---}\!\!\left|\begin{array}{l} \longrightarrow \text{increased charge delocalization in } R'^- \\ \longrightarrow \text{increased basicity of crossover X} \\ \longrightarrow \text{increased crossover p}K_a\text{ values} \end{array}\right. \qquad (25)$$

Although the ionic character of the carbon–lithium bond is expected to increase greatly in changing from alkyl- and aryl- to phenylethynyllithium (the pK_a values of ethane, benzene, and phenylacetylene, are, respectively, 42, 37, and 18.5),[10] crossover X and crossover pK_a are the same for reaction series I, II, and III. Also, the pK_a of diphenylmethane[10] is ~35. These facts indicate that the emphasis on charge delocalization in (25) is justified.

Comparison of reaction series V and VI shows that the increased steric requirement engendered by the α-methyl substituent does not affect crossover. Comparison of V and VII shows that benzyllithium and allyllithium are very similar in their stereochemical behavior with R_3Si^*X.

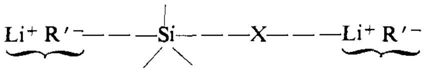
Although data for stereochemical reaction series involving Grignard reagents are quite limited, due to lesser reactivity of RMgX compared to R'Li, consideration of reactions 21–24 indicates that the general trends in scheme 25 apply also to the reactions of R_3Si^*X with Grignard reagents. Thus, the change from an alkylmagnesium halide to a benzylmagnesium halide changes the stereochemistry of reaction of R_3Si^*OMe from *retention* to *inversion* of configuration.

Mechanism Models. Previous discussion[2] of the mechanistic significance of the stereochemical results obtained from reactions of R_3Si^*Cl and R_3Si^*F with R'Li led to the conclusion that (26) and (27) comprise reasonable models for the *inversion* reactions of R_3Si^*Cl with alkyl- and aryllithium, and for the *inversion* reactions of R_3Si^*F and R_3Si^*Cl with benzyl-type organolithium reagents. In the structures given below it must be emphasized that *the R'Li units may or may not be components of larger $(R'Li)_n$ aggregates. Also, donor solvent molecules are not shown.*



$$\mathrm{Li{-}{-}{-}R'{-}{-}{-}Si{-}{-}{-}Cl{-}{-}{-}LiR'} \qquad (26)$$

R' = alkyl or aryl



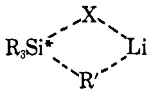
$$\underbrace{\mathrm{Li^+\,R'^-}}_{\text{ion pair}}\mathrm{{-}{-}{-}Si{-}{-}{-}X{-}{-}{-}}\underbrace{\mathrm{Li^+\,R'^-}}_{\text{ion pair}} \qquad (27)$$

R' = benzyl-type (charge-delocalized) group

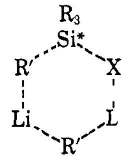
For the *inversion* reactions of OMe in the present work, reaction series V–VIII, transition-state structure 27 (X = OMe) seems reasonable. With R'Li reagents in which negative charge can be highly delocalized in R'^-, the Li^+ counterion will be an effective electrophile for removal of the highly basic OMe leaving group. Apparently, high ionic character of the carbon–lithium bond is not sufficient of itself to bring about operation of mechanism 27. High ionic character of R'Li and charge delocalization in R'^- are both necessary. For PhC≡CLi, R'Li must be a "tight" ion pair in which the localized negative charge in an sp orbital makes the Li^+ counterion a poorer electrophile than Li^+ in charge-delocalized R'Li reagents.[11] The more basic the leaving group, X, the more electrophilic R'Li must be to provide an *inversion* path.

For the very basic H leaving group, *inversion* of configuration demands very high electrophilicity of Li^+ and mechanism 28 operates only in reaction series VIII with Ph_2CHLi.

In accord with previous discussion of the *retention* reactions of R_3Si^*F with alkyl- and aryllithium, the following possible SNi-Si transition-state structures are proposed for the *retention* reactions of OMe and H in the present work. In (28) and (29) breaking of Si–X and breaking of Li–C are mutually helpful in promoting formation of Si–C and LiX. Mechanisms 28 and/or 29 operate when R'Li cannot of itself provide sufficient electrophilic assistance needed for removal of basic leaving groups by mechanism 27. In concerted bond-making, bond-breaking mechanisms 28 and 29 high electrophilicity of Li in the organolithium reagent is not as critical a factor.



(28)



(29)

In transition-state structures 28 and 29 over-all geometry about the silicon center may be approximately trigonal bipyramid or tetragonal pyramid.[2,12]

Table II and scheme 25 provide strong evidence for the general hypothesis that the majority of the reactions of R_3SiX with strong nucleophiles have transition states in which the "bonds" to the entering and leaving groups are long and weak relative to the Si–R bonds. *The data in Table II are not at all consistent with critical involvement of Si-5 intermediates, $(R_3R'SiX)^-Li^+$, containing five full bonds to silicon.*

Experimental Section

With the exception of *o*-tolyllithium, details of the preparation of the organolithium and Grignard reagents used in this study have been reported previously.[2]

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[10] See ref 8.

[11] For studies on charge delocalization in benzyl-type R'Li reagents, see, for example: V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963); R. Waack and M. A. Doran, *ibid.*, **85**, 1651 (1963), and subsequent papers by Waack and co-workers.

[12] For a detailed discussion of the geometry of SNi-Si transition states, see: L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N.Y., 1965, Chapter 3.

Reactions with Benzhydryllithium. An ethereal solution of (−)-α-naphthylphenylmethylmethoxysilane (1.53 g, 0.0054 mole) with $[\alpha]_D$ −16.5° (*c* 10.2, pentane)[6] was added to approximately 100 ml of benzhydryllithium (0.4 *N*) and the mixture stirred for 20 min. Following work-up,[2] analysis of the product indicated a slight trace of α-naphthylphenylmethylsilanol in addition to the desired product and diphenylmethane. The diphenylmethane was separated from the silanes by distillation, and the silanol separated by elution chromatography over a 26 × 1 in. column of silica gel using a benzene–pentane solvent blend. Removal of the solvent and crystallization from heptane gave (−)-α-naphthylphenylbenzhydrylmethylsilane (0.47 g, 0.0013 mole) with $[\alpha]_D$ −16.7° (*c* 2.0, chloroform) and mp 118–120°. Recrystallization from heptane afforded 0.42 g of the benzhydrylsilane with $[\alpha]_D$ −17.5° (*c* 2.2, chloroform).[2]

The reaction between benzhydryllithium and (+)-α-naphthylphenylmethylsilane (4.99 g, 0.020 mole), $[\alpha]_D$ +33.4° (*c* 5.2, pentane),[6] was performed under different conditions. After mixing the organolithium reagent and the silane, the reaction temperature was maintained at 45° for 10 days. An infrared spectrum of the crude product indicated that a large quantity of the unchanged silane was still present. It was separated from the benzhydrylsilane by a two-step process: fractional distillation to remove the major portion of the silane and then a chemical sequence, the chlorination of silane, the hydrolysis of the chlorosilane to the silanol, and the absorption of the silanol on silica gel, to remove the last trace of the silane. The residue (1.14 g) remaining after chromatography and removal of solvent had $[\alpha]_D$ +3.7° (*c* 5.5, chloroform). The infrared spectrum of this material was identical with that of the authentic benzhydrylsilane.[2] After several crystallizations from heptane (+)-α-naphthylphenylbenzhydrylmethylsilane (0.12 g) was obtained with mp 121–123° and $[\alpha]_D$ +17.1° (*c* 1.2, chloroform).

Reactions with Benzyllithium. A solution of (−)-α-naphthylphenylmethylmethoxysilane (2.30 g, 0.0083 mole), $[\alpha]_D$ −22.7° (*c* 13.1, ethyl ether), in ethyl ether (25 ml) was added to an ethereal solution of benzyllithium, prepared by the lithium metal cleavage of benzyl methyl ether (6.3 g).[2] Following a 4-hr reaction period, the reaction mixture was hydrolyzed and the crude product was chromatographed over a 26 × 1 in. column of silica gel with a benzene–pentane blend. Subsequent removal of solvent gave (−)-α-naphthylphenylbenzylmethylsilane (2.05 g, 0.0059 mole), $[\alpha]_D$ −3.9° (*c* 6.0, pentane). The material was characterized by the infrared spectrum.[2]

The reaction with (−)-α-naphthylphenylmethylsilane (4.39 g, 0.0177 mole), $[\alpha]_D$ −34.2° (*c* 3.0, pentane), was performed in a similar manner except that the reaction mixture was maintained at 35° for 14 hr before it was hydrolyzed. (+)-α-Naphthylphenylbenzylmethylsilane (4.26 g, 0.0126 mole), $[\alpha]_D$ +5.50° (*c* 3.5, pentane), was obtained.

The reaction with (−)-α-naphthylphenylmethyl-(−)-menthoxysilane (4.54 g, 0.0113 mole), $[\alpha]_D$ −54.2° (*c* 18.2, ethyl ether),[6] was maintained at 35° for 24 hr. (+)-α-Naphthylphenylbenzylmethylsilane (3.14 g, 0.0093 mole), $[\alpha]_D$ +2.4° (*c* 17.0, pentane), was obtained after fractional distillation.

Reaction with Benzylmagnesium Chloride. A solution of (−)-α-naphthylphenylmethylmethoxysilane (2.58 g, 0.0093 mole), $[\alpha]_D$ −16.5° (*c* 10.0, pentane), in ethyl ether (25 ml) was added to benzylmagnesium chloride prepared from benzyl chloride (14 g) and magnesium (5.0 g) in ethyl ether (50 ml). The reaction mixture was maintained at 35° for 3 days and then raised to 70° for an 18-hr period. After hydrolysis and fractional distillation (−)-α-naphthylphenylbenzylmethylsilane (1.37 g, 0.0041 mole), $[\alpha]_D$ −3.3° (*c* 5.4, pentane), was recovered.

Reactions with α-Methylbenzyllithium. The organolithium reagent was prepared in ethyl ether solvent following the procedure described earlier.[2] (+)-α-Naphthylphenylmethylmethoxysilane (2.94 g, 0.0102 mole), $[\alpha]_D$ +21.2° (*c* 13.2, ethyl ether), was mixed with α-methylbenzyllithium, prepared from bis(α-methylbenzyl) ether (9.0 g), for 2 hr at ambient temperature before the reaction mixture was hydrolyzed. The crude product was eluted through a column of silica gel with a benzene–pentane solvent blend. Removal of the solvent gave (−)-α-naphthylphenyl-(α-methylbenzyl)-methylsilane (2.44 g, 0.0069 mole) with $[\alpha]_D$ −13.9° (*c* 11.5, pentane). The material was characterized by the infrared spectrum.[2]

The procedure for the coupling reaction with (−)-α-naphthylphenylmethyl-(−)-menthoxysilane (6.43 g, 0.016 mole), $[\alpha]_D$ −54.2° (*c* 18.2, ethyl ether), was similar to that described above except that the reaction time was extended to 9 days and the temperature gradually raised to 70°. Hydrolysis and chromatography left a product which was contaminated by the unchanged menthoxysilane. The menthoxysilane was then reduced with lithium aluminum hydride to the silane and the desired material separated from the silane by fractional distillation. (−)-α-Naphthylphenyl-(α-methylbenzyl)methylsilane (0.96 g, 0.0026 mole), $[\alpha]_D$ −25.2° (*c* 4.6, pentane), was obtained.

Reaction with (−)-α-naphthylphenylmethylsilane (3.00 g, 0.012 mole), $[\alpha]_D$ −35.1° (*c* 1.9, pentane), for a period of 24 hr gave (−)-α-naphthylphenyl-(α-methylbenzyl)methylsilane with $[\alpha]_D$ −25.2° (*c* 4.6, pentane). When tetrahydrofuran was used as the solvent, the reaction between the organolithium reagent, prepared from bis-(α-methylbenzyl) ether (11.7 g), and (−)-α-naphthylphenylmethylsilane (3.0 g, 0.012 mole) was maintained for 18 hr at ambient temperature before hydrolysis. (−)-α-Naphthylphenyl-(α-methylbenzyl)methylsilane (2.01 g, 0.0057 mole), $[\alpha]_D$ −4.2° (*c* 8.0, pentane), was obtained after fractional distillation.

Reactions with *p*-Methoxybenzyllithium. The reagent was prepared in ethyl ether from the lithium metal cleavage of di-*p*-anisyl ether (8.3 g) by the procedure described earlier.[2] Reaction with (−)-α-naphthylphenylmethylmethoxysilane (1.67 g, 0.0060 mole), $[\alpha]_D$ −20.1° (*c* 7.3, ethyl ether), for 2 hr at ambient temperature gave (+)-α-naphthylphenyl-(*p*-methoxybenzyl)methylsilane (0.62 g, 0.0017 mole), $[\alpha]_D$ +11.3° (*c* 3.0, ethyl ether), bp 200–210° (0.6 mm) after fractional distillation. The material was characterized by the infrared spectrum.[2]

Reaction with (+)-α-naphthylphenylmethylsilane (3.01 g, 0.0122 mole), $[\alpha]_D$ +36.3° (*c* 13.0, ethyl ether), for 24 hr at 35° gave (−)-α-naphthylphenyl-(*p*-methoxybenzyl)methylsilane (2.68 g, 0.0073 mole) with $[\alpha]_D$ −15.9° (*c* 11.1, ethyl ether) following fractional distillation.

Reactions with Allyllithium. The reagent was prepared in ethyl ether solvent from tetraallyltin (7.0 g) and *n*-butyllithium as previously described.[2] To the reagent was added (+)-α-naphthylphenylmethylmethoxysilane (4.15 g, 0.0149 mole), $[\alpha]_D$ +22.0° (*c* 16.7, ethyl ether). The reaction mixture was hydrolyzed after a reaction period of 30 min in the usual manner,[2] except that hydrochloric acid was not used. (−)-α-Naphthylphenylallylmethylsilane (2.17 g, 0.0075 mole) with $[\alpha]_D$ −2.1° (*c* 11.5, pentane) and bp 156–160° (0.6 mm) was obtained by fractional distillation of the crude product. The material was characterized by the infrared spectrum.[2]

The reaction between allyllithium and (−)-α-naphthylphenylmethylsilane (4.0 g, 0.0162 mole), $[\alpha]_D$ −35.5° (*c* 9.4, pentane), gave (−)-α-naphthylphenylallylmethylsilane (3.45 g, 0.012 mole) with $[\alpha]_D$ −10.1° (*c* 22.7, pentane) and bp 160–165° (1.0 mm) after hydrolysis and fractional distillation.

Reaction with Phenylethynyllithium. The reagent was prepared in ethyl ether solvent from phenylacetylene (5.0 g) and *n*-butyllithium. To the organolithium reagent was added a solution of (+)-α-naphthylphenylmethylmethoxysilane (4.60 g, 0.0169 mole), $[\alpha]_D$ +21.3° (*c* 18.1, ethyl ether), in ethyl ether. After a reaction period of approximately 14 hr, the mixture was hydrolyzed and the crude product chromatographed over a column of silica gel with a benzene–pentane solvent blend. Fractional distillation gave (−)-α-naphthylphenyl(phenylethynyl)methylsilane (2.13 g, 0.0066 mole), $[\alpha]_D$ −9.1° (*c* 6.9, pentane) and bp 200–205° (0.8 mm).

By the above procedure, (−)-α-naphthylphenylmethylfluorosilane (0.94 g, 0.0035 mole), $[\alpha]_D$ −44.3° (*c* 3.6, ethyl ether), gave, after a reaction period of 4 hr, (+)-α-naphthylphenyl(phenylethynyl)methylsilane (1.12 g, 0.0033 mole) with $[\alpha]_D$ +6.9° (*c* 5.8, pentane).

By the above procedure, (+)-α-naphthylphenylmethylchlorosilane (1.10 g, 0.0039 mole), $[\alpha]_D$ +6.0° (*c* 5.0, pentane), gave, after a reaction period of 1 hr, (−)-α-naphthylphenyl(phenylethynyl)-methylsilane (0.85 g, 0.0024 mole) with $[\alpha]_D$ −8.6° (*c* 4.9, pentane). The infrared spectra for the products from R_3Si^*OMe, R_3Si^*F, and R_3Si^*Cl were identical and had the bands characteristic of the α-naphthylphenylmethylsilyl group[6] and also had bands at 3.45, 4.68, 6.75, 6.95, 9.34, and 10.9 μ attributed to the phenylethynyl group on Si.

Anal. Calcd for $C_{25}H_{20}Si$: C, 85.7; H, 5.98; Si, 8.06. Found: C, 86.1; H, 5.94; Si, 8.05.

Reactions with *o*-Tolyllithium. The organolithium reagent was prepared by slowing adding a solution of *o*-chlorotoluene (12.0 g) in dry ethyl ether (100 ml) to a mixture, rapidly stirred and heated to reflux, of lithium metal wire (2.0 g), cut into $^1/_8$-in. lengths, and ethyl ether (250 ml). Following a reaction period of 4 hr, the reaction mixture was cooled and a dense white solid allowed to settle. The clear pale yellow solution of *o*-tolyllithium was separated from the excess lithium metal and other solid material by means of nitrogen pressure. Titration of an aliquot with 0.1 *N* hydrochloric acid indicated that the solution contained 0.075 mole of reagent. A solution of (+)-α-naphthylphenylmethylchlorosilane (2.35 g, 0.0083 mole), $[\alpha]_D$ +5.9° (*c* 16.8, pentane), in ethyl ether (5 ml) was added to the reagent. The reaction mixture was stirred for 14 hr before it was hydrolyzed following the usual procedure. The crude product was chromatographed over silica gel with a solvent blend of benzene and pentane. Removal of solvent under vacuum left a pale orange-yellow gum (2.74 g) which had $[\alpha]_D$ +17.6° (*c* 10.5, pentane). Crystallization from pentane at 0° gave very pale yellow crystals of α-naphthyl-(*o*-tolyl)phenylmethylsilane (1.90 g, 0.0054 mole) with mp 102–103° and $[\alpha]_D$ +23.0° (*c* 7.0, pentane). Recrystallization from pentane gave essentially white crystals with mp 103–105° and $[\alpha]_D$ +23.2° (*c* 1.0, pentane). The infrared spectrum had the bands characteristic of the α-naphthylphenylmethylsilyl group as well as strong bands at 6.90, 7.80, 8.85, and 9.25 μ attributed to the *o*-tolyl group on silicon.

Anal. Calcd for $C_{22}H_{22}Si$: C, 85.2; H, 6.55; Si, 8.30. Found: C, 85.4; H, 6.61; Si, 8.52.

Reaction between *o*-tolyllithium and (+)-α-naphthylphenylmethylmethoxysilane (2.97 g, 0.0107 mole), $[\alpha]_D$ +5.7° (*c* 11.0, pentane), under similar conditions to those described above except that the temperature was maintained for 16 hr at 35° gave (+)-α-naphthyl-(*o*-tolyl)phenylmethylsilane (3.50 g, 0.0103 mole) with $[\alpha]_D$ +7.5° (*c* 15.0, pentane). Crystallization from pentane gave white crystals, mp 94–107° and $[\alpha]_D$ +11.7° (*c* 0.6, pentane).

Reactions with Ethyllithium and *n*-Propyllithium.[13] The reaction of R_3Si^*OMe with ethyllithium has been described previously.[2]

Optically pure (+)-α-naphthylphenylmethylsilane (0.89 g, 0.0036 mole) dissolved in 10 ml of pentane was mixed with a solution of *n*-propyllithium (2.35 g, 0.0470 mole) in 42 ml of pentane. As the flask was heated pentane vapor was allowed to escape until the flask temperature reached 82°. After 4 hr at 82° (conditions more vigorous than those required for Cl, F, and OMe leaving groups), workup and chromatography over silica gel gave (+)-α-naphthylphenyl-*n*-propylmethylsilane (1.01 g), $[\alpha]_D$ +1.7° (*c* 5.52, pentane), having an infrared spectrum identical with that of the authentic substance.[2]

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(13) These reactions were carried out by P. G. Rodewald.

Stereochemistry of Asymmetric Silicon. IX. The Silicon–Sulfur Bond[1,2]

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Contribution from the Departments of Chemistry, University of California, Davis, California, and The Pennsylvania State University, University Park, Pennsylvania. *Received May 10, 1967*

Abstract: Optically active compounds containing silicon–sulfur bonds, R_3Si^*SR', have been synthesized. Relative and absolute configurations have been assigned to these substances which contain the α-naphthylphenylmethylsilyl group, α-NpPhMeSi*. The stereochemistry of their reactions with diverse reagents has been studied and is compared with the stereochemistry of R_3Si^*OR' reactions. The general mechanistic significance of the results is discussed and mechanism models are proposed.

Previous papers[1,4–10] in this series on the stereochemistry of substitution at asymmetric silicon, exemplified[9] by the α-NpPhMeSi* system, designated R_3Si^* below, have involved a variety of leaving groups: alkoxy and siloxy,[1,5,8] carboxylate and tosylate,[6] halogen,[4–8] and nitrogen.[10] In the present paper we extend our stereochemical studies to sulfur leaving groups, using R_3Si^*SR' compounds, where R′ = H, CH_3, R_3Si^*.[11]

In spite of general chemical interest in the organosilicon–sulfur bond[12] no mechanistic information concerning this bond has been available. This situation, plus the stereochemical importance of comparing the silicon–sulfur bond with the silicon–oxygen bond, suggested the present work.

Syntheses and Stereochemical Correlation of Configuration. Crystalline (+)-1,3-di-α-naphthyl-1,3-diphenyl-1,3-dimethyldisilthiane [(+)-$R_3Si^*SSi^*R_3$ (I)] was prepared by reaction of (−)-R_3Si^*Cl with H_2S and Et_3N in pentane solvent. Methanolysis of the (+)-disilthiane I in ether solvent in the presence of Et_2NH gave the known (+)-$R_3Si^*OCH_3$ in high optical purity due to highly stereospecific breaking of the first silicon–sulfur bond in I. The other product, formed without breaking of the second silicon–sulfur bond, is (+)-diethylammonium α-naphthylphenylmethylsilylmercaptide (II). This salt[13] conveniently precipitates from the reaction mixture as fluffy white crystals.

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(1) For the preceding paper in this series, see L. H. Sommer and W. D. Korte, *J. Am. Chem. Soc.*, **89**, 5802 (1967).

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