acid indicated that the solution contained 0.075 mole of reagent. A solution of (+)-α-naphthylphenylmethylchlorosilane (2.35 g, 0.0083 mole), [α]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 [α]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 [α]D +23.0° (*c* 7.0, pentane). Recrystallization from pentane gave essentially white crystals with mp 103–105° and [α]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), [α]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 [α]D +7.5° (*c* 15.0, pentane). Crystallization from pentane gave white crystals, mp 94–107° and [α]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), work-up and chromatography over silica gel gave (+)-α-naphthylphenyl-*n*-propylmethylsilane (1.01 g), [α]D +1.7° (*c* 5.52, pentane), having an infrared spectrum identical with that of the authentic substance.[2]

Acknowledgment. We thank the Dow Corning Corporation for generous support.

[13] These reactions were carried out by P. G. Rodewald.

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

Leo H. Sommer[3] and Jerome McLick

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).

[2] In its initial stages this work was supported by Dow Corning Corporation. Later work was supported by Grant GP-5662 from the National Science Foundation.

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

[5] L. H. Sommer, C. L. Frye, and G. A. Parker, *ibid.*, **86**, 3276 (1964).

[6] L. H. Sommer, G. A. Parker, and C. L. Frye, *ibid.*, **86**, 3280 (1964).

[7] L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *ibid.*, **89**, 857 (1967).

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

[9] L. H. Sommer, K. W. Michael, and W. D. Korte, *ibid.*, **89**, 868 (1967).

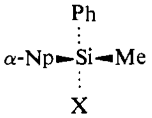
[10] L. H. Sommer and J. D. Citron, *ibid.*, **89**, 5797 (1967).

[11] For a preliminary communication see L. H. Sommer and J. McLick, *J. Am. Chem. Soc.*, **88**, 5359 (1966).

[12] For reviews see (a) C. Eaborn, "Organosilicon Compounds," Butterworth & Co. (Publishers) Ltd., London, 1960, pp 333–338; (b) V. Bažant and V. Chavalovský, "Organosilicon Compounds," Vol. 1, Academic Press Inc., New York, N. Y., 1965, pp 72–75; (c) A. Haas, *Angew. Chem.*, 77, 1066 (1965).

[13] Secondary amine salts of aromatic thiols are known: G. F. Grillot and T. J. Brooks, Jr., *J. Am. Chem. Soc.*, 72, 4281 (1950).

Table I. α-NpPhMeSi*X Compounds Having the Configuration



$$\begin{array}{c} Ph \\ \vdots \\ \alpha\text{-}Np\blacktriangleright Si \blacktriangleleft Me \\ \vdots \\ X \end{array}$$

Si*X[a]	[α]D, deg (solvent)	Si*X	[α]D, deg (solvent)
(*S*)-(−)-$R_3Si^*SSi^*R_3$	−101 (hexane)	(*R*)-(+)-R_3Si^*H	+34 (pentane)
(*S*)-(−)-$R_3Si^*S^-Et_2NH_2^+$	−52 (benzene)	(*S*)-(−)-R_3Si^*Cl	−6.3 (pentane)
(*S*)-(−)-R_3Si^*SH	−26 (pentane)	(*S*)-(+)-R_3Si^*OH	+21 (ether)
(*S*)-(−)-$R_3Si^*SCH_3$	−12 (pentane)	(*S*)-(+)-$R_3Si^*OCH_3$	+17 (pentane)

[a] Names for the above optically active silicon–sulfur compounds, in order of listing, are: (*S*)-(−)-1,3-di-α-naphthyl-1,3-diphenyl-1,3-dimethyldisilthiane; (*S*)-(−)-diethylammonium α-naphthylphenylmethylsilylmercaptide; (*S*)-(−)-α-naphthylphenylmethylsilylthiol; (*S*)-(−)-α-naphthylphenylmethyl(methylthio)silane.

$$\underset{[\alpha]_D\ +34^\circ}{2(+)\text{-}R_3Si^*H} \xrightarrow[a]{Cl_2} \underset{[\alpha]_D\ -6.3^\circ}{2(-)\text{-}R_3Si^*Cl} \xrightarrow[b]{H_2S,\ Et_3N} \underset{I,\ [\alpha]_D\ +101^\circ}{(+)\text{-}R_3Si^*SSi^*R_3}$$

$$\underset{II,\ [\alpha]_D\ +52^\circ}{(+)\text{-}R_3SiS^-Et_2NH_2^+} + \underset{[\alpha]_D\ +17^\circ}{(+)\text{-}R_3Si^*OCH_3} \xleftarrow[c]{CH_3OH,\ Et_2NH} \qquad (1)$$

Methanolysis product (+)-$R_3Si^*OCH_3$ is known to have the (+)-R_3Si^*H configuration,[4] indicating over-all retention of configuration for the conversion of R_3Si^*H to $R_3Si^*OCH_3$ in reaction sequence 1. Moreover, since reaction 1a is known to proceed with retention of configuration,[4] reactions 1b and 1c must be either both inversions or both retentions. Consistently predominant inversion stereochemistry for reactions of R_3Si^*Cl with a wide variety of nucleophiles including water and alcohols and alcoholate ions[7,14] and the SN2-Si stereochemistry rule for good leaving groups point to inversion for (1b), and hence also for (1c), as being most reasonable. Further evidence for correct assignment of inversion for reactions 1b and 1c is provided by stereochemical results reported below.

Reaction of 1 equiv of HCl with the (+)-amine salt II in benzene results in precipitation of $Et_2NH_2^+Cl^-$ and liberation of (+)-α-naphthylphenylmethylsilylthiol [(+)-R_3Si^*SH (III)] which can be crystallized from pentane.

$$\underset{II,\ [\alpha]_D\ +52^\circ}{(+)\text{-}R_3Si^*S^-Et_2NH_2^+} + HCl \xrightarrow{\text{benzene}} \underset{III,\ [\alpha]_D\ +26^\circ}{(+)\text{-}R_3Si^*SH} + Et_2NH_2^+Cl^- \qquad (2)$$

Reaction of the (+)-amine salt II with methyl iodide gives $Et_2NH_2^+I^-$ and (+)-α-naphthylphenylmethyl(methylthio)silane [(+)-$R_3Si^*SCH_3$ (IV)] which also can be crystallized from pentane.

$$\underset{II,\ [\alpha]_D\ +52^\circ}{(+)\text{-}R_3Si^*S^-Et_2NH_2^+} + CH_3I \xrightarrow{\text{pentane–ether}} \underset{IV,\ [\alpha]_D\ +12^\circ}{(+)\text{-}R_3Si^*SCH_3} + Et_2NH_2^+I^- \qquad (3)$$

Because formation of II, III, and IV from the disilthiane I does not involve the asymmetric center, all four compounds have the same configuration, as well as the same sign of optical rotation. Based on an inversion path for reaction 1b given above, Table I assigns absolute configuration to these new compounds, together with that rigorously established for the parent (+)-R_3Si^*H,[4] and for other pertinent compounds.[4] An alternate method for the preparation of R_3Si^*SH and $R_3Si^*SCH_3$ is shown below. The procedure is described in the Experimental Section as method b.

$$Et_2NH + H_2S \xrightarrow{\text{pentane}} HS^-Et_2NH_2^+ \xrightarrow[\text{excess } Et_2NH]{(-)\text{-}R_3Si^*Cl} \underset{\text{mixed salts}}{(+)\text{-}R_3Si^*S^-Et_2NH_2^+ + Et_2NH_2^+Cl^-}$$

$$Et_2NH_2^+X^- + (+)\text{-}R_3Si^*SR' \xleftarrow{HCl \text{ or } CH_3I}$$

Stereochemistry of the Silicon–Sulfur Bond. Organosilicon–sulfur bonds are considerably more reactive than comparable carbon–sulfur bonds, and they are especially reactive toward basic reagents. In the present paper, reactions of the Si–S bond with $LiAlH_4$, water, methanol, and organolithium reagents are reported.

In ether solvent, $LiAlH_4$ reduction of the first Si–S bond in $R_3Si^*SSi^*R_3$ is fast at room temperature and proceeds with inversion of configuration. As a result of this reaction, the second Si–S bond is in a mercaptide salt structure, approximated by $R_3SiS^-(LiAlH_3)^+$, V, which is essentially inert to reduction at room temperature. Upon acidic work-up, V is converted to the conjugate silylthiol which can be separated from product R_3Si^*H by precipitation of the amine salt.

$$\underset{I,\ [\alpha]_D\ +101^\circ}{(+)\text{-}R_3Si^*SSi^*R_3} + LiAlH_4 \xrightarrow[\substack{Et_2O \\ \text{inversion}}]{22^\circ,\ 30 \text{ min}} \underset{[\alpha]_D\ +34^\circ}{(+)\text{-}R_3Si^*H} + \underset{V}{[R_3Si^*S^-(LiAlH_3)^+]} \qquad (4a)$$

$$V \xrightarrow{\text{HCl work-up}} \underset{\text{in product mixture}}{[(+)\text{-}R_3Si^*SH]} \xrightarrow{Et_2NH} \underset{[\alpha]_D\ +51^\circ}{(+)\text{-}R_3Si^*S^-Et_2NH_2^+} \qquad (4b)$$

Structure V can be independently prepared by mixture of (+)-R_3Si^*SH with $LiAlH_4$ at −78°, and while inert at room temperature, it can be reduced by heating at 85° in butyl ether. This reaction proceeds with retention of configuration.

$$(+)\text{-}R_3Si^*SH + LiAlH_4 \xrightarrow[-H_2]{-78^\circ} \xrightarrow[24 \text{ hr}]{\text{room temp}}$$

$$V \xrightarrow[\substack{Et_2O\text{–}Bu_2O \\ \text{retention}}]{85^\circ,\ 24 \text{ hr}} \underset{[\alpha]_D\ -30^\circ}{(-)\text{-}R_3Si^*H} \qquad (5)$$

Total reduction of (+)-$R_3Si^*SSi^*R_3$, achieved by following reaction 4a with heating at 85°, combines the above results by yielding *racemic* R_3Si^*H. Table II summarizes the foregoing $LiAlH_4$ reduction stereo-

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[14] L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, Chapter 4.

Table II. $LiAlH_4$ Reduction of R_3Si^*SR' Compounds

Reaction no.	Reactant	Temp, °C	Product	Stereo-specificity[a]
4a	$(+)\text{-}R_3Si^*SSi^*R_3$	22	$(+)\text{-}R_3Si^*H$	100% inv
5	$R_3Si^*S^-(LiAlH_3)^+$ [b]	85	$(-)\text{-}R_3Si^*H$	93% ret
6	$(+)\text{-}R_3Si^*S^-Et_2NH_2^+$	85	$(-)\text{-}R_3Si^*H$	81% ret
7	$(+)\text{-}R_3Si^*SCH_3$	22	$(+)\text{-}R_3Si^*H$	92% inv

[a] A stereospecificity of, say, 90% means that the product was 80% optically pure (20% racemic) if optically pure reactant was used. [b] As derived from $(+)\text{-}R_3Si^*SH$.

Table III. Hydrolysis and Methanolysis Reactions of R_3Si^*SR' Compounds

Reaction no.	Reactants[b,c]	Products	Stereospecificity[a]
8[d]	$(+)\text{-}R_3Si^*SSi^*R_3 + H_2O$	$(+)\text{-}R_3Si^*OH + (+)\text{-}R_3Si^*S^-Et_2NH_2^+$	97% inv
1c[d]	$(+)\text{-}R_3Si^*SSi^*R_3 + CH_3OH$	$(+)\text{-}R_3Si^*OCH_3 + (+)\text{-}R_3Si^*S^-Et_2NH_2^+$	100% inv
9[d]	$(+)\text{-}R_3Si^*SCH_3 + H_2O$	$(+)\text{-}R_3Si^*OH$	100% inv
10[d]	$(+)\text{-}R_3Si^*SCH_3 + CH_3OH$	$(+)\text{-}R_3Si^*OCH_3$	99% inv
11	$(+)\text{-}R_3Si^*SH + H_2O$	$(+)\text{-}R_3Si^*OH$	94% inv
12	$(+)\text{-}R_3Si^*SH + CH_3OH$	$(\pm)\text{-}R_3Si^*OCH_3$	Racemic product
13[e]	$(+)\text{-}R_3Si^*S^-Et_2NH_2^+ + CH_3OH$	$(+)\text{-}R_3Si^*OCH_3$	82% inv

[a] Refer to corresponding footnote in Table II. [b] In some cases the enantiomer was used and gave the enantiomer of the product listed. [c] Ether solvent except as noted. [d] Reaction in presence of ≥ 1 equiv of Et_2NH. [e] Reaction medium 1:2 $CH_3OH\text{-}Et_2O$ (v/v).

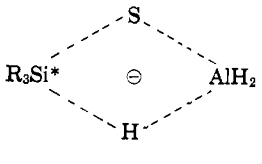
chemistry, together with results obtained for reduction of $(+)\text{-}R_3Si^*S^-Et_2NH_2^+$ and $(+)\text{-}R_3Si^*SCH_3$.

Reasoning based on the general rule of inversion of configuration for nucleophilic displacement of good leaving groups X from R_3Si^*X[7] clearly would predict inversion for reaction 4a (pK_a of leaving group conjugate acid, R_3Si^*SH, ~7)[15] and retention for reaction 5 (second pK_a for H_2S is 14), *based on the fact of opposite stereochemical paths for these two reactions.* This consistency reinforces the absolute configurational assignments given in Table I.

Conversely, Table II shows, by inversion of configuration for reaction 7, that CH_3S^- is a better leaving group than S^{2-}, which is consistent with decreased basicity of CH_3S^- (pK_a of CH_3SH is 10)[16] relative to S^{2-}.[17]

The foregoing stereochemical results allow assignment of reaction mechanisms for $LiAlH_4$ reductions of R_3Si^*SR'. Inversion of configuration for displacement of $R_3Si^*S^-$ and CH_3S^- from silicon by hydride (reactions 4a and 7) would be the natural result of SN2-Si mechanism operation commonly favored by good leaving groups and strong nucleophiles.[7] SN2-Si rate-controlling transition-state geometry is trigonal bipyramidal with apical entering and leaving groups whose bonds to central silicon are longer and weaker than those of the equatorial nonreacting organic (R) groups. Greater apical bond length is the result of considerable ionic stretching, which is strongly implied by sensitivity of both reaction stereochemistry and reaction rate to leaving group basicity.[7] In this regard, faster reaction rate for hydride displacement of $R_3Si^*S^-$ than for significantly more basic CH_3S^- is noted to be consistent with previous observations of reaction rate dependence on leaving group basicity,[18] *i.e.*, increased ability of leaving group to bear a negative charge results in increased reaction rates with strong nucleophiles.

The predominant retention stereochemistry which obtains for hydride displacement of S^{2-} (reactions 5 and 6 in Table II) is considered an example of the SNi-Si mechanism,[19] and is pictured below. It is analogous to that previously formulated for the retentive $LiAlH_4$



reduction of R_3Si^*OH.[5] With its provision for electrophilic assistance and minimization of charge separation, the SNi-Si mechanism commonly operates for polar displacement of poor leaving groups from silicon in nonpolar media.

Table III reports the stereochemical results obtained for hydrolysis and methanolysis reactions of the optically active silicon-sulfur compounds.

Hydrolysis and methanolysis reactions of $R_3Si^*SSi^*R_3$ and $R_3Si^*SCH_3$ are catalyzed by Et_2NH. Under amine catalysis conditions, hydrolysis and methanolysis of $R_3Si^*SSi^*R_3$ (reactions 8 and 1c) are complete in minutes, while under comparable conditions, the corresponding reactions of $R_3Si^*SCH_3$ take hours (reactions 9 and 10). This reaction rate difference is, in all likelihood, mainly due to leaving group basicity difference, and the implications of this concerning transition-state structure were noted above in connection with $LiAlH_4$ reduction rate difference.

Hydrolysis and methanolysis of free R_3Si^*SH in Et_2O are comparatively slow (hours), and are not catalyzed by dilute acid. Methanolysis of $R_3SiS^-Et_2NH_2^+$, which is of low solubility in Et_2O, was carried out in 1:2 $CH_3OH\text{-}Et_2O$ medium.

All of the hydrolysis and methanolysis reactions listed in Table III are inversions, and as such are assigned SN2-Si mechanism pathways. The base catalysis observed for reactions of $R_3Si^*SSi^*R_3$ and $R_3Si^*SCH_3$ can be interpreted as being the result of hydrogen bonding between the amine catalyst and the hydroxylic hydrogen of water or methanol. This would increase the nucleophilic character of the attacking oxygen center, and

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(15) A pK_a value of approximately 7 for R_3Si^*SH can be inferred from the fact that R_3Si^*SH parallels aromatic thiols (pK_a values known to be *ca.* 7) in its ability to form amine salts. In contrast, aliphatic thiols (pK_a values > 10) do not form amine salts due to insufficient acidity. See A. A. Oswald and T. J. Wallace in "The Chemistry of Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, Inc., Oxford, 1966, p 207. Also, silanols are known to be more acidic than corresponding carbinols (see ref 12a, pp 95–96), and in all likelihood a parallel obtains for silylthiols *vs.* carbon thiols.

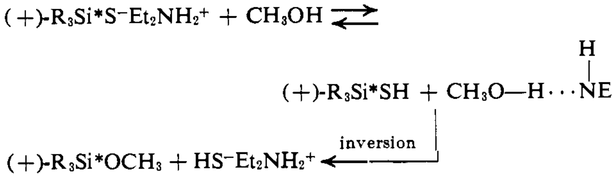
(16) M. M. Kreevoy, *et al.*, *J. Org. Chem.*, **29**, 1641 (1964).

(17) The actual leaving group may approximate H_3AlS^-, but inductive electron release from aluminum to sulfur should still cause such a leaving group to be more basic than RS^-.

(18) Reference 14, Chapter 8.

(19) Reference 14, Chapter 11.

thus increase reaction rate. For the special case of methanol solvolysis of $R_3Si^*S^-Et_2NH_2^+$, the actual displacement reaction may or may not be preceded by an acid–base equilibrium involving the free thiol.



$$(+)\text{-}R_3Si^*S^-Et_2NH_2^+ + CH_3OH \rightleftarrows (+)\text{-}R_3Si^*SH + CH_3O\text{—}H\cdots\overset{H}{N}Et_2 \xrightarrow{\text{inversion}} (+)\text{-}R_3Si^*OCH_3 + HS^-Et_2NH_2^+ \qquad (14)$$

A reaction sequence such as (14) would favor inversion since it provides a good leaving group (HS^-). However, other recent studies in this laboratory[20] have shown that *in polar solvents* "poor" leaving groups of even greater basicity than S^{2-} (*i.e.*, pK_a of $HX > 14$) can be displaced with inversion of configuration, and this may be the case for displacement of S^{2-}. With our present data, a distinction between these possibilities cannot be made.

Although hydrolysis of R_3Si^*SH is seen to proceed with inversion (reaction 11), the corresponding methanolysis yields racemic R_3Si^*OMe (reaction 12) in ether or in methanol solvent. The cause of this racemization is not known, but a likely possibility is a faster racemization rate for product R_3Si^*OMe than for thiol methanolysis, under the reaction conditions. R_3Si^*OMe is known to be optically unstable under mildly acidic conditions.[21]

Reactions 15, 16, and 17 below are the first stereochemical results for reactions of R_3Si^*SR' with organometallic reagents.

Reaction of (+)-disilthiane (I) with excess neo pentyllithium, *neo*-$C_5H_{11}Li$, in ether solvent at room temperature cleaves the first Si–S bond with inversion of configuration,[22] and generates the lithium mercaptide VI, containing the second Si–S bond. This latter product is converted to the conjugate silylthiol upon acidic work-up, and this can be recovered from the reaction mixture as the diethylamine salt. This scheme is analogous to (4b) given above.

$$(+)\text{-}R_3Si^*SSi^*R_3 + neo\text{-}C_5H_{11}Li \xrightarrow[\text{room temp inversion}]{Et_2O} (-)\text{-}R_3Si^*\text{-}neo\text{-}C_5H_{11} + [R_3Si^*S^-Li^+] \qquad (15)$$

Reaction of the methylthiosilane with neopentyllithium gives retention of configuration under the same conditions.

$$(+)\text{-}R_3Si^*SCH_3 + neo\text{-}C_5H_{11}Li \xrightarrow[\text{room temp retention}]{Et_2O} (+)\text{-}R_3Si\text{-}neo\text{-}C_5H_{11} + CH_3S^-Li^+ \qquad (16)$$

However, reaction of the methylthiosilane with benzyllithium proceeds with inversion of configuration.

$$(+)\text{-}R_3Si^*SCH_3 + PhCH_2Li \xrightarrow[\text{inversion}]{Et_2O} (-)\text{-}R_3Si^*CH_2Ph + CH_3S^-Li^+ \qquad (17)$$

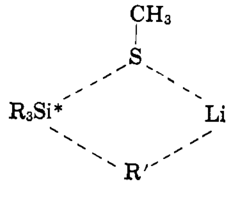
Referring to the invertive displacement of $R_3Si^*S^-$ and the retentive displacement of CH_3S^- by neopentyllithium seen in reactions 15 and 16, this contrasting stereochemistry is most likely the result of leaving group basicity difference. $LiAlH_4$ reduction, hydrolysis, and methanolysis reactions are all inversions for displacement of CH_3S^- as well as $R_3Si^*S^-$. For those reactions, the leaving group basicity difference only manifests itself in faster reaction rate for displacement of the less basic leaving group ($R_3Si^*S^-$). For reaction with neopentyllithium, leaving group basicity becomes most critical to reaction stereochemistry, with the more basic leaving group (CH_3S^-) now leaving with retention of configuration.

Similar comparative stereochemistry for the reaction of simple alkyllithium reagents with R_3Si^*Cl *vs.* R_3Si^*F has been previously observed and discussed.[8] In this regard the stereochemical behavior of R_3Si^*SMe resembles that of R_3Si^*F which undergoes displacement of F^- by (1) $LiAlH_4$ with inversion,[4] (2) simple alkyllithium reagents with retention, and (3) charge-delocalized organolithium reagents with inversion of configuration.[8] Displacement of CH_3S^- follows the same stereochemistry in all three categories. Inversion for the reaction of $R_3Si^*SCH_3$ with a charge-delocalized organolithium reagent, $PhCH_2Li$, is demonstrated by reaction 17 above.

The preferred inversion of configuration and faster reaction rates for reactions of $R_3Si^*SSi^*R_3$ *vs.* $R_3Si^*SCH_3$ are taken to be primarily due to leaving group basicity difference, as mentioned above.

For reactions of R_3Si^*X with organolithium reagents, there has been previous discussion on the dependence of stereochemistry on leaving group ability and the nature of the carbon–lithium bond of the organolithium reagent.[8] An SN2–Si mechanism has been proposed for invertive displacement of Cl^- from R_3Si^*Cl by simple alkyllithium reagents $R'Li$.[8] By analogy, this mechanism applies to reaction 15 (displacement of $R_3Si^*S^-$).

An SNi–Si mechanism has been proposed for the retentive displacement of F^- from R_3Si^*F by $R'Li$,[8] and, by analogy, this mechanism applies to reaction 16 (displacement of CH_3S^-). It is pictured in its simplest form below.



$R' = neo\text{-}C_5H_{11}\text{–}$

Comparison of the Silicon–Oxygen Bond with the Silicon–Sulfur Bond. The first direct comparison of R_3Si^*OR' stereochemistry with R_3Si^*SR' stereochemistry is provided by $LiAlH_4$ reduction reactions. Both Si–O bonds in $R_3Si^*OSi^*R_3$ undergo reduction upon prolonged heating above 100° and proceed with *retention* of configuration,[5] whereas the first Si–S bond in $R_3Si^*SSi^*R_3$ undergoes complete reduction at 22° in 30 min, and with *inversion* of configuration. The second Si–S bond, as $Si\text{–}S^-$, is able to undergo reduction at 85° with *retention* of configuration. Also, reduction of R_3SiOCH_3[4] goes with *retention*, while that for $R_3Si^*SCH_3$ goes with *inversion* of configuration under similar reaction conditions.

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(20) Unpublished work of L. H. Sommer, W. D. Korte, and H. Fujimoto.

(21) R. Baker, R. W. Bott, C. Eaborn, and P. W. Jones, *J. Organometal. Chem.* (Amsterdam), 1, 37 (1963).

(22) Absolute configurational assignments for R_3Si^*-*neo*-C_5H_{11} and $R_3Si^*CH_2(C_6H_5)$ are given in ref 8.

$R_3Si*OSi*R_3$ is unaffected by the presence of CH_3OH and Et_2NH in ether solvent, while $R_3Si*SSi*R_3$ undergoes rapid methanolysis under those conditions (reaction 1c) and with *inversion* of configuration.

Also $R_3Si*OSi*R_3$[23] and $R_3Si*OCH_3$[1] react with simple alkyllithium reagents with *retention*, but $R_3Si*SSi*R_3$ does so with *inversion* of configuration.

The striking change in reaction stereochemistry caused by substitution of sulfur for oxygen in R_3Si*OR' gives dramatic support to the general concept of *inversion* of configuration being favored by better (*less basic*) leaving groups, while *retention* of configuration commonly obtains for displacement of poorer (*more basic*) leaving groups in nonpolar media.

The previous[7] general correlation of reaction stereochemistry of R_3Si*X with leaving group basicity, rather than leaving group electronegativity, receives striking confirmation from the present studies of the silicon–sulfur bond. Clearly, any hypothesis which attributes *inversion* stereochemistry of R_3Si*X to high electronegativity of X and consequent preference of X for an apical position in an Si-5 intermediate[24] is refuted by the present results.

Experimental Section[25]

Preparation of (+)-1,3-Di-α-naphthyl-1,3-diphenyl-1,3-dimethyldisilthiane, (+)-$R_3Si*SSi*R_3$. A solution of 5.76 g (20.4 mmoles) of (−)-R_3Si*Cl, $[\alpha]_D$ −6.3°, in 150 ml of purified pentane was combined with a solution of 2.29 g (25 mmoles) of Et_3N in 40 ml of pentane. H_2S was immediately bubbled into the solution, and moderately fast gas flow was maintained for 30 min, during which time precipitated amine hydrochloride gradually accumulated. The mixture was allowed to sit for 2 hr and then filtered. The retained precipitate was washed with 50 ml of boiling hexane and the filtered wash solution combined with the original filtrate. The resultant solution was evaporated down to about 75 ml and, upon cooling, product crystals appeared. After several hours the product was collected and recrystallized from hot hexane, yielding 2.3 g of crystals (43% yield), mp 115–116°, $[\alpha]_D$ +101° (*c* 0.5, hexane). The infrared spectrum in CCl_4 showed all of the absorption bands characteristic of the R_3Si* system[4] plus a band at 20 μ attributed to the Si–S bond.[26]

Anal. Calcd for $C_{34}H_{30}Si_2S$: C, 77.51; H, 5.74; Si, 10.66; S, 6.08. Found: C, 77.26; H, 5.43; Si, 10.85; S, 6.22.

Preparation of (+)-Diethylammonium α-Naphthylphenylmethylsilylmercaptide (Methanolysis of (+)-$R_3Si*SSi*R_3$). A solution of 1.20 g (2.28 mmoles) of (+)-$R_3Si*SSi*R_3$, $[\alpha]_D$ +101° (*c* 0.4, hexane), in 60 ml of dry ethyl ether was prepared in a 125-ml flask equipped with a magnetic stirrer. Using rapid stirring, 0.6 ml of Et_2NH and 0.36 ml of methanol were syringed into the solution. After several seconds, the product precipitated. After stirring the mixture several minutes, the crystalline material was collected on a Büchner funnel and washed well with purified pentane (the filtrate is retained since it contains co-product $R_3Si*OCH_3$). The yield was 0.76 g (47% of total Si) of the fluffy, white salt, $[\alpha]_D$ +52° (*c* 0.7, benzene), mp 105–130° dec. A sample recrystallized from CCl_4 gave an infrared spectrum showing the bands characteristic of the R_3Si* system, with some distortion, plus new bands at 3.8 and 4.1 μ attributable to the $Et_2NH_2^+$ moiety.[27] Recrystallization did not increase optical purity, and optical purity was not consistent for all preparations. The salt is sensitive to air, but can be stored under vacuum.

Anal. Calcd for $C_{21}H_{27}NSiS$: C, 71.33; H, 7.70; N, 3.96; Si, 7.94; S, 9.07. Found: C, 70.97; H, 7.48; N, 4.06; Si, 7.88; S, 9.18.

The filtrate from the above product collection was stripped of solvent, excess amine, and alcohol; the residue was taken up in pentane and filtered. Removal of pentane yielded 0.56 g (44% of total Si) of white solid, $[\alpha]_D$ +17° (*c* 2.24, pentane), whose infrared spectrum was identical with that of authentic $R_3Si*OCH_3$.[4]

Preparation of (+)-α-Naphthylphenylmethylsilylthiol, R_3Si*SH. Method a. A solution of 1.56 g (4.42 mmoles) of (+)-$R_3SiS^-Et_2NH_2^+$, $[\alpha]_D$ +52° (*c* 0.4, benzene), was prepared in 60 ml of purified benzene. Into this solution was syringed 15.3 ml of a benzene–HCl solution known to be 0.29 *M* in HCl. Immediate precipitation of $Et_2NH_2^+Cl^-$ (0.45 g, 96% yield, identified by melting point) resulted. After filtration, the solution was stripped of benzene; the residue was taken up in pentane and then refiltered. The product crystallized after concentration of the pentane solution, yielding 1.1 g (89% yield) of crystals with mp 63–64°, $[\alpha]_D$ +26° (*c* 1.0, pentane). An infrared spectrum in CCl_4 showed the characteristic R_3Si* system absorbances, plus a band at 3.95 μ due to the S–H stretch,[26] and a band at 20 μ due to the Si–S bond.[26]

Anal. Calcd for $C_{17}H_{16}SiS$: C, 72.81; H, 5.75; S, 11.43. Found: C, 72.85; H, 5.90; S, 11.64.

Method b. H_2S gas was bubbled into a solution of 3.4 ml of Et_2NH in 100 ml of purified pentane contained in a 250-ml flask. There soon appeared $HS^-Et_2NH_2^+$ precipitate, and bubbling was continued for 5 min. This was followed by addition of a second 3.4-ml portion of Et_2NH, and with fast magnetic stirring a solution of 6.8 g (24 mmoles) of (−)-R_3Si*Cl, $[\alpha]_D$ −5.9°, in 50 ml of pentane, was added to the mixture. A thick mixture of precipitated salts, (+)-$R_3Si*S^-Et_2NH_2^+$ and $Et_2NH_2^+Cl^-$, resulted. After stirring for several minutes, the mixed salts were collected on a Büchner funnel and washed profusely with pentane. The material was transferred to a 250-ml flask, and a slurry was made by addition of 100 ml of purified pentane. Anhydrous HCl was bubbled into this mixture for 4 min, during which time the slurry had considerably thinned. The mixture, containing free (+)-R_3Si*SH in solution, was filtered into a 250-ml suction flask, and after removal of solvent and vacuum pumping gave 4.1 g of crude product. Crystallization from a concentrated pentane solution gave 3.7 g (55% yield) of (+)-R_3Si*SH, $[\alpha]_D$ +26°, mp 63–64°, with correct infrared spectrum.

Preparation of (+)-α-Naphthylphenylmethyl(methylthio)silane, (+)-$R_3Si*SCH_3$. Method a. A slurry of 2.6 g (7.35 mmoles) of (+)-$R_3Si*S^-Et_2NH_2^+$, $[\alpha]_D$ +52° (*c* 0.4, benzene), in 90 ml of purified pentane and 50 ml of dry ether was combined with 9 ml of CH_3I and the mixture magnetically stirred for 16 hr, during which time it had thinned considerably. The solid $Et_2NH_2^+I^-$ (identified by melting point after recrystallization from methanol–ethyl acetate) was filtered off, and the filtrate was stripped of solvent and excess CH_3I. The residue (2.1 g, 97% yield) was taken up in pentane, and crystallization of white product took place from a concentrated solution in the refrigerator. After two crystallizations, 1.2 g (55%) of solid (+)-$R_3Si*SCH_3$, mp 57–59°, $[\alpha]_D$ +12° (*c* 2.0, pentane), was obtained. An infrared spectrum in CCl_4 showed the expected R_3Si* system peaks, plus a new band at 3.45 μ due to $S–CH_3$, and the Si–S band at 19.8 μ. A pmr spectrum showed, in addition to aromatic proton signals downfield, two equal-area singlets: at 0.9 ppm (relative to TMS) due to $Si–CH_3$ protons, and at 1.8 ppm due to $S–CH_3$ protons.

Anal. Calcd for $C_{18}H_{18}SiS$: C, 73.41; H, 6.16; S, 10.89. Found: C, 73.48; H, 6.34; S, 10.70.

Method b. Referring to the method b preparation of R_3Si*SH above, a second batch of mixed salts made from 24 mmoles of (−)-R_3Si*Cl, $[\alpha]_D$ −6.3°, was stirred with 10 ml of CH_3I in 90 ml of purified pentane and 50 ml of dry ether for 14 hr. The mixture, which had become considerably thinner, was filtered, then stripped of solvent, yielding 5.20 g of crude product. Crystallization was made difficult by silanol impurity (about 10% by infrared analysis) and so the material was chromatographed on a 18 × 0.5 in. silica gel column with elution by approximately 100 ml of pentane–benzene (50:50 by volume). The liquid product (3.10 g) had $[\alpha]_D$ +11.8° (*c* 1.1, pentane) and had an infrared spectrum identical with that of authentic $R_3Si*SCH_3$. Crystallization from a concentrated pentane solution gave 2.70 g (38% yield) of (+)-$R_3Si*SCH_3$, $[\alpha]_D$ +12.3° (*c* 0.8, pentane), mp 57–59°.

Lithium Aluminum Hydride Reductions. 1. (+)-$R_3Si*SSi*R_3$. A solution of 1.00 g (1.9 mmoles) of (+)-$R_3Si*SSi*R_3$, $[\alpha]_D$ +101° (*c* 0.4, hexane), in 30 ml of dry ether was combined with a mixture of 1.20 g of $LiAlH_4$ in 90 ml of ether. The mixture was allowed to sit for 24 hr whereupon excess $LiAlH_4$ was decomposed by slow addition of acetone, and the mixture was worked up with a combination of ice, 100 ml of pentane, and 10 ml of concentrated HCl

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[23] L. H. Sommer and W. D. Korte, unpublished work.

[24] An Si-5 intermediate has been defined as containing five full bonds to silicon.[8]

[25] Analyses by Schwarzkopf Microanalytical Laboratory. Melting points are uncorrected.

[26] A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960).

[27] B. Chenon and C. Sandorfy, *Can. J. Chem.*, **36**, 1181 (1958).

in a separatory funnel. After washing the organic layer to neutral, drying over sodium sulfate, and stripping of solvent, an infrared spectrum of the residue showed approximately 50% R_3Si^*H formed, as well as the presence of R_3Si^*SH and R_3Si^*OH. The residue was taken up in 20 ml of pentane, and with rapid magnetic stirring 2 mmoles of Et_2NH was added, causing precipitation of (+)-$R_3Si^*S^-Et_2NH_2^+$ (0.51 g, 38% of total Si), $[\alpha]_D$ +51° (*c* 0.52, benzene). The remaining solution was chromatographed over a 18 × 0.5 in. silica gel column, eluting with pentane–benzene (80:20 by volume), yielding 0.39 g (42% of total Si) of (+)-R_3Si^*H, $[\alpha]_D$ +34° (*c* 1.6, pentane), whose infrared spectrum coincided with that of authentic R_3Si^*H.[4]

2. **Total Reduction of (+)-$R_3Si^*SSi^*R_3$.** A solution of 0.36 g (0.67 mmole) of (+)-$R_3Si^*SSi^*R_3$, $[\alpha]_D$ +101°, in 10 ml of ether was combined with a mixture of 0.40 g of $LiAlH_4$ in 30 ml of ether in a 200-ml, three-necked flask equipped with condenser, thermometer, and heating mantle. The mixture was allowed to stand 24 hr, and then 40 ml of di-*n*-butyl ether was added. The mixture was heated, and diethyl ether was allowed to escape until the temperature reached 85°, whereupon the condenser was cooled for reflux and the system was maintained at 85° for 24 hr. Excess hydride was decomposed by acetone, and the reaction mixture was worked up with 10 ml of concentrated HCl, ice, and ether. After washing to neutral and drying over sodium sulfate, removal of solvent yielded 0.308 g (91%) of (±)-R_3Si^*H, $[\alpha]_D$ 0° (*c* 1.2, pentane) within experimental error, which gave the expected infrared spectrum.

3. **(+)-R_3Si^*SH.** In a three-necked flask equipped with a condenser and a Gilman trap, a solution of 0.387 g (1.38 mmoles) of (+)-R_3Si^*SH, $[\alpha]_D$ +26°, in 20 ml of ethyl ether was cooled in a Dry Ice–acetone bath. To this solution was added a solution of 0.400 g of $LiAlH_4$ in 20 ml of ether which was also at Dry Ice–acetone temperature, and the mixture was kept at that temperature for 30 min, over which time slow bubbling was observed, and taken to be hydrogen gas. The mixture was then allowed to warm up to room temperature, accompanied by an increase in the bubbling rate, which gradually subsided, and the mixture was allowed to sit at ambient temperature for 24 hr. After the addition of di-*n*-butyl ether (40 ml) the flask was heated to 85° (ethyl ether allowed to escape) and maintained for 24 hr. The mixture was worked up as in the previous experiment. The crude product (0.34 g), $[\alpha]_D$ −23.4°, was contaminated by a small amount of starting material. Chromatography over silica gel with elution by pentane–benzene (80:20 volume) yielded 0.245 g (72%) of pure (−)-R_3Si^*H, $[\alpha]_D$ −30° (*c* 0.98, pentane), identified by its infrared spectrum.

In a separate experiment carried out as above, except with heating at 85° omitted, the starting silylthiol was recovered with a trace of reduction.

4. **(+)-$R_3Si^*S^-Et_2NH_2^+$.** A mixture of 0.580 g (1.64 mmoles) of (+)-$R_3Si^*S^-Et_2NH_2^+$, $[\alpha]_D$ +52° (*c* 0.4, benzene), 40 ml of ethyl ether, and 40 ml of butyl ether was prepared in a 200-ml flask equipped for heating. The salt remained mostly undissolved, but when 0.400 g of $LiAlH_4$ was added, the amine salt went rapidly into solution, accompanied by bubbling. The mixture was heated, with ethyl ether escape, to 85° and maintained at that temperature for 24 hr. The reaction mixture was worked up as for above experiments and dried over sodium sulfate. An infrared spectrum of the crude product showed it to be predominantly R_3Si^*H but contaminated with a small amount of Si–S impurity. Chromatography over silica gel in the usual manner for R_3Si^*H purification gave 0.31 g (76%) of (−)-R_3Si^*H, $[\alpha]_D$ −21.0° (*c* 1.2, pentane), with the expected infrared spectrum.

5. **(+)-$R_3Si^*SCH_3$.** A solution of 0.50 g (1.70 mmoles) of (+)-$R_3Si^*SCH_3$, $[\alpha]_D$ +12° (*c* 2.0, pentane), in 5 ml of anhydrous ether was combined with 0.6 g of $LiAlH_4$ in 30 ml of ether, and the mixture was refluxed for 24 hr. After the usual work-up and drying of reaction product, it was chromatographed over silica gel to give 0.295 g (70%) of (+)-R_3Si^*H, $[\alpha]_D$ +29° (*c* 1.18, pentane), identified by its infrared spectrum.

A later experiment determined that for the same reagent concentrations, reduction is actually 40% complete in 1 hr at room temperature.

Hydrolysis Reactions. 1. (+)-$R_3Si^*SSi^*R_3$. A solution of 1.20 g (2.28 mmoles) of (+)-$R_3Si^*SSi^*R_3$, $[\alpha]_D$ +101°, and 0.5 ml of Et_2NH in 20 ml of ethyl ether was shaken with 25 ml of H_2O in a separatory funnel. There immediately appeared a thick, white precipitate. Addition of water and pentane to the mixture, with additional shaking, gave separation of phases, with the precipitate suspended in the organic layer. It was collected by suction filtration, dried under vacuum, and identified by its infrared spectrum as (+)-$R_3Si^*S^-Et_2NH_2^+$, $[\alpha]_D$ +49° (*c* 0.4, benzene), 0.645 g (40% of total Si). The ethereal filtrate obtained above was stripped of solvent, and an infrared spectrum showed the intense broad band at 3.0 μ plus the other bands characteristic of R_3Si^*OH.[4] The silanol had $[\alpha]_D$ +19° (*c* 2.5, ether), yield 0.625 g (52% of total Si).

2. **(+)-$R_3Si^*SCH_3$.** A solution of 0.500 g (1.70 mmoles) of (+)-$R_3Si^*SCH_3$, $[\alpha]_D$ +10.5°, and 0.18 ml of Et_2NH in 5.0 ml of ether was magnetically stirred with 2 ml of H_2O for 24 hr. The reaction mixture, which smelled of methanethiol, was separated and the ethereal solution dried over sodium sulfate, then stripped of solvent and amine. The 0.445 g of residue (99% yield), $[\alpha]_D$ +18.3° (*c* 1.78, ether), was identified as (+)-R_3Si^*OH by its infrared spectrum.

3. **(+)-R_3Si^*SH.** A solution of 0.400 g (1.43 mmoles) of (+)-R_3Si^*SH, $[\alpha]_D$ +26° (*c* 0.8, pentane), in 5.0 ml of ether was magnetically stirred with 3 ml of H_2O for 36 hr. The ethereal solution was separated, dried over sodium sulfate, and yielded 0.380 g (100% yield) of (+)-R_3Si^*OH, $[\alpha]_D$ +17.6° (*c* 1.5, ether). The product was identified by its infrared spectrum which, in addition to the broad, intense Si–OH peak at 3.0 μ, indicated a small amount of starting material as impurity.

Methanolysis Reactions. 1. (+)-$R_3Si^*SSi^*R_3$. Refer to preparation of (+)-$R_3Si^*S^-Et_2NH_2^+$ above.

2. **(+)-$R_3Si^*SCH_3$.** A solution of 0.47 g (1.6 mmoles) of (+)-$R_3Si^*SCH_3$, $[\alpha]_D$ +10.5°, 0.65 ml of CH_3OH, and 0.17 ml of Et_2NH was made in 5.0 ml of dry ethyl ether and allowed to stand protected from the atmosphere for 12 hr. Over this time the solution developed the odor of methanethiol. The solvent and excess reagents were removed under vacuum, leaving 0.43 g (97% yield) of (+)-$R_3Si^*OCH_3$, $[\alpha]_D$ +14.7° (*c* 1.7, pentane). The material had an infrared spectrum identical with that of authentic $R_3Si^*OCH_3$.

3. **(+)-R_3Si^*SH.** A solution of 0.320 g (1.14 moles) of (+)-R_3Si^*SH, $[\alpha]_D$ +26°, and 0.073 g of CH_3OH was prepared in 1.0 ml of dry ethyl ether, and the solution was allowed to sit for 36 hr protected from the atmosphere. Removal of solvent under vacuum gave 0.306 g (97% yield) of (±)-$R_3Si^*OCH_3$, $[\alpha]_D$ 0° (*c* 1.2, pentane), which gave the expected infrared spectrum for $R_3Si^*OCH_3$. Previous experiments had shown the reaction to be slow and accompanied by extensive racemization. Reaction in both hexane and neat methanol also gave racemic product.

4. **(+)-$R_3Si^*S^-Et_2NH_2^+$.** A mixture of 10 ml of CH_3OH and 20 ml of ethyl ether was added to 0.78 g (2.2 mmoles) of (+)-$R_3Si^*S^-Et_2NH_2^+$, $[\alpha]_D$ +51°, which quickly went into solution. The solution smelled of H_2S and gradually took on a yellow color. After 2 hr the ether and excess methanol were removed under vacuum. When the solid residue was taken up in pentane, a yellow impurity was left behind. The colorless pentane solution yielded 0.596 g (97% yield) of (+)-$R_3Si^*OCH_3$, $[\alpha]_D$ +13.1° (*c* 2.3, pentane). The product had an infrared spectrum the same as that of authentic $R_3Si^*OCH_3$.

Reaction of (+)-$R_3Si^*SSi^*R_3$ with Neopentyllithium. Freshly prepared neopentyllithium (~30 mmoles in 30 ml of ethyl ether) was added to a solution of 1.20 g (2.28 mmoles) of (+)-$R_3Si^*SSi^*R_3$, $[\alpha]_D$ +99.7° (*c* 0.4, hexane), in 15 ml of ether under a nitrogen atmosphere. The mixture, which took on a light yellow color, was stirred at ambient temperature for 16 hr and was worked up with 5 ml of concentrated hydrochloric acid, 30 ml of ice water, and 30 ml of ether in a separatory funnel. The acidified organic layer was washed with water until neutral, dried over sodium sulfate, and then stripped of solvent. An infrared spectrum of the crude product showed presence of approximately 50% SiOH and SiSH impurity. The mixture was chromatographed on a 18 × 0.5 in. silica gel column with elution by pentane–benzene (70:30 by volume). A total of 0.579 g (40% of total Si) of material whose infrared spectrum was identical with that of authentic R_3Si^*-*neo*-C_5H_{11}[3] was obtained, and this product had $[\alpha]_D$ −24.3° (*c* 0.83, pentane).

In another experiment set up exactly as above, except starting with 1 g of (+)-$R_3Si^*SSi^*R_3$, the crude product mixture was dissolved in 60 ml of purified pentane; 1 equiv of Et_2NH was added with fast magnetic stirring, which precipitated 0.30 g of (+)-$R_3Si^*S^-Et_2NH_2^+$, $[\alpha]_D$ +42°, accounting for 14% of total Si. Infrared analysis showed the remaining product to be a mixture of silanol and (−)-R_3Si^*-*neo*-C_5H_{11} in expected proportions.

Reaction of (+)-$R_3Si^*SCH_3$ with Neopentyllithium. To a solution of 0.588 g (2 mmoles) of (+)-$R_3Si^*SCH_3$, $[\alpha]_D$ +11.4°, in 5 ml of ethyl ether was added 30 mmoles of neopentyllithium in 30 ml of ether. The mixture, which turned to a light yellow color, was stirred for 24 hr at room temperature. Work-up with acid (see previous experiment) followed by washing to neutrality and drying over sodium sulfate yielded, after solvent removal, 0.656 g of crude product, $[\alpha]_D$ +25.3° (c 2.6, pentane), which was contaminated by a small amount of silanol. Chromatography on a 18 × 0.5 in. silica gel column with elution by pentane–benzene (70:30) gave 0.400 g (63% yield) of (+)-R_3Si^*-*neo*-C_5H_{11}, $[\alpha]_D$ +28.5° (c 1.6, pentane), identified by its infrared spectrum.

Reaction of (+)-$R_3Si^*SCH_3$ with Benzyllithium. A solution of 0.426 g (1.45 mmoles) of (+)-$R_3Si^*SCH_3$, $[\alpha]_D$ +10.5°, in 7 ml of dry ethyl ether, was added over 1 min to a rapidly stirred solution of 6 mmoles of benzyllithium[8] in 30 ml of ethyl ether. The addition caused the red color of the lithium reagent solution to diminish somewhat, and the solution was allowed to stand at ambient temperature for 10 hr. Acidic work-up (see previous experiment) followed by drying over sodium sulfate and removal of solvent gave 1.07 g of colorless product mixture. This mixture was taken up in pentane and chromatographed on a 18 × 0.5 in. silica gel column. Elution was effected by 125 ml of pentane–benzene (60:40 by volume), yielding 0.376 g (77% yield) of (−)-$R_3Si^*CH_2Ph$, $[\alpha]_D$ −2.4° (c 2.8, pentane) and $[\alpha]_D$ +3.2° (c 2.7, cyclohexane).[8] The infrared spectrum of the viscous product was identical with that of authentic $R_3Si^*CH_2Ph$.[8] Correcting for optical impurity of the starting material, the reaction proceeded with a stereospecificity of 70% inversion.

Protonation of the Indole Grignard Reagent and Other Organometallic Derivatives of Indole[1]

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Abstract: Alkali metal derivatives of indole protonate predominantly on nitrogen. The Grignard reagent on the other hand gave carbon protonation when intermediate amounts of D_2O were added. Addition of very large or very small amounts of D_2O yielded either N-protonation or no reaction followed by N-protonation in the work-up. The effects of concentration, solvent, and heterogeneity on the amount of carbon protonation of the indole Grignard reagent are described. The results are discussed in terms of the structure of the organometallic derivatives of indole and the mechanism of their protonation.

Ten years after the discovery of alkylmagnesium halides by Grignard, Oddo found that indole and ethylmagnesium iodide reacted in diethyl ether with the evolution of ethane to produce the indole Grignard reagent (indolylmagnesium iodide).[3] This Grignard reagent undergoes many of the reactions characteristic of simple alkylmagnesium halides, such as carbonation, alkylation, and acylation.[4,5] The products formed are substituted predominantly at the 3 position of the indole ring, although small amounts of 1-substituted and 1,3-disubstituted products have been reported. This selectivity in substitution reactions has led to the widespread use of the indole Grignard reagent in the synthesis of naturally occurring and pharmacologically important substances.[6]

Since its discovery, the structure of the indole Grignard reagent has been the subject of considerable controversy mainly as a result of its substitution behavior. The indole Grignard reagent is alkylated and carbonated predominantly at the 3 position,[7] while alkali metal derivatives of indole yield mostly 1-substituted products. This has led to the formulation of the Grignard reagent variously as an N–MgX or a C–MgX species. Recently two studies of the alkylation of organometallic derivatives of indole have been reported.[8,9] The Grignard reagent reacts with methyl iodide in THF or toluene to give exclusively skatole, while the alkali metal derivatives (Li, Na, K) give varying amounts of skatole and 1-methylindole. The data suggest that increased dissociation of the organometallic derivatives of indole leads to 1-alkylated products, while associated salts yield 3-alkyl products. Thus factors which increase the ability of these organometallic indole derivatives to dissociate, such as an increase in solvent polarity, increasing homogeneity of the reaction mixture, and increasing electropositive character of the metal ion, tend to produce more N-alkylation.[9] This hypothesis is in agreement with results obtained in the alkylation of alkali metal salts of pyrrole[10,11] and other ambident anions.

Recent nmr investigations of the organometallic derivatives of indole have cast much light upon their structures.[9,12,13] The C–MgX formulation (**2**) for the

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(2) National Science Foundation Undergraduate Research Participant, 1964.

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