drazide, azide, and oxazolidone to I-d_6 as described for the undeuterated compounds.[4,6] The reactions with sodium phenoxide[16] and phenol (and work-up) were carried out exactly as described above for I. The results are listed in Table I. The result of a similar experiment involving I and C_6H_5OD[17] is also listed in Table I.

Acknowledgment. We thank Professors Jack Hine and Paul Gassman for interesting discussions concerning mechanisms of these reactions, and Mr. Wei Liang for the preparation and characterization of VI.

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[16] W. R. Boehme, "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 592. The sodium phenoxide, further dried by distilling benzene from it, did not liberate gas when treated with sodium hydride.

[17] M. Charpentier-Morize, M. Mayes, and B. Tchoubar, *Bull. Soc. Chim. Fr.*, 529 (1965).

Optically Active Silyl- and Germylmethyllithium Reagents and the Stereochemistry of Carbene Insertions into the Silicon–Hydrogen and Germanium–Hydrogen Bonds

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Abstract: The preparations of three optically active metalloidal–methyllithium reagents 1-NpPhMeMCHR′Li (M = Si, R′ = H or Ph; M = Ge, R′ = H) of known absolute configuration are described. These reagents have been used to determine the stereochemistry of the following reactions: the insertion of dibromocarbene into the SiH and GeH bonds; the insertion of carbethoxycarbene into the SiH bond; the thermal rearrangement of $R_3Si^*CH_2CO_2H$ and $R_3Si^*CHPhCO_2H$; and the base-catalyzed rearrangement of $R_3Si^*CHPhCO_2H$. In addition, the establishment of the absolute configuration and maximum specific rotation of R_3Ge^*Et now makes possible the unambiguous assignment of the stereochemistries of a number of reactions at asymmetric germanium.

In a recent publication several methods of preparing silyl- and germylmethyllithium reagents were reported and it was shown that use of the halogen–metal exchange reaction between *n*-butyllithium and α-bromosilanes and -germanes was a generally applicable route of considerable synthetic value.[1] This work has now been extended to some related optically active organolithium compounds and this paper describes the preparation and some applications of three such 1-naphthylphenylmethylmetalloidal reagents to stereochemical problems.

$$R_3M^*CH_2Br \xrightarrow{n\text{-BuLi}} R_3M^*CH_2Li, \quad M = Si, Ge$$

$$R_3Si^*CH_2Ph \xrightarrow{n\text{-BuLi-TMEDA}} R_3Si^*CHPhLi$$

Interest in this work arose from a desire to study the rearrangements of silylacetic acids (for which R_3Si^*-$CHR'Li$ were obvious precursors) to their related acetoxysilanes.[2] However, since the reagents have known absolute configurations at the metalloid atom and can be prepared in high yield with nearly 100% optical purity, it is apparent that they will prove to be valuable intermediates for stereochemical studies in general, since their achiral analogs undergo a variety of reactions with different types of substrates (*e.g.*, carbon dioxide, alkyl iodides, cyanogen, ethyl chloroformate, and carbonyl compounds[1,3]) yielding β-functional organometalloids.

The 1-naphthylphenylmethylsilyl- and -germylmethyllithium reagents were prepared, as described previously for achiral substrates,[1] by insertion of dibromocarbene into the optically active silane, R_3Si^*H, or germane, R_3Ge^*H. While the dibromo compounds

$$R_3M^*H \xrightarrow{PhHgCBr_3} R_3M^*CHBr_2 \xrightarrow[2.\ HBr]{1.\ n\text{-BuLi}} R_3M^*CH_2Br \xrightarrow{n\text{-BuLi}} R_3M^*CH_2Li$$

R_3M^* = 1-NpPhMeSi or 1-NpPhMeGe

were in each case liquids, the monobromomethylsilane and -germane, the immediate precursors to the organolithium reagents, were crystalline solids. This was important because it was then possible to crystallize these to optical purity as judged by constant specific rotation. At the time this work was initiated it had been shown by Ritter and Sommer[4] that insertion of dibromocarbene into the SiH bond of R_3Si^*H gave an optically active product and it appeared possible from these studies to establish the stereochemistry of this insertion reaction using the reactions shown above as part of a Walden cycle. More recently, Sommer, *et al.*,[5] have shown that the insertion involves retention of configuration with high stereospecificity by correlating the configurations of 1-naphthylphenylmethyldibromo-

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* To whom correspondence should be addressed.

[1] A. G. Brook, J. M. Duff, and D. G. Anderson, *Can. J. Chem.*, **48**, 561 (1970). For a recently described alternative route to the monohalomethyl precursors see D. Seyferth and S. P. Hopper, *J. Organometal. Chem.*, 23, 99 (1970).

[2] A. G. Brook, D. G. Anderson, and J. M. Duff, *J. Amer. Chem. Soc.*, 90, 3876 (1968).

[3] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p 394.

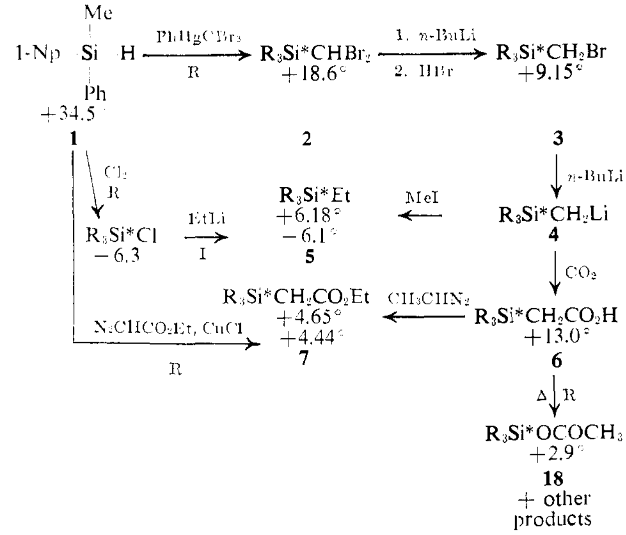
[4] A. Ritter and L. H. Sommer, Abstracts of First International Symposium on Organosilicon Chemistry, Prague, Czechoslovakia, Aug 1965, p 279.

[5] L. H. Sommer, L. A. Ulland, and A. Ritter, *J. Amer. Chem. Soc.*, 90, 4486 (1968).

methylsilane (or its dichloro analog) as obtained by two different routes. The present work completely confirms their results.

The absolute configurations of the organosilicon compounds used in the present studies were established by the Walden cycle shown in Scheme I. Using the general conditions described by Seyferth[6] and more recently applied by Sommer,[5] optically pure (+)-1-naphthylphenylmethylsilane (I) was converted with tribromomethylphenylmercury to the dibromo compound II, an oil having $[\alpha]_D$ +18.6°. This was converted by halogen–metal exchange, followed by treatment with anhydrous hydrogen bromide, to the monobromo compound **3**, which initially had a specific rotation of +8.7°. This compound was recrystallized to a constant melting point and a maximum specific rotation of +9.15°. Upon treatment with *n*-butyllithium, **3** readily underwent halogen–metal exchange to give the organolithium reagent **4** which was derivatized in two ways.

Scheme I



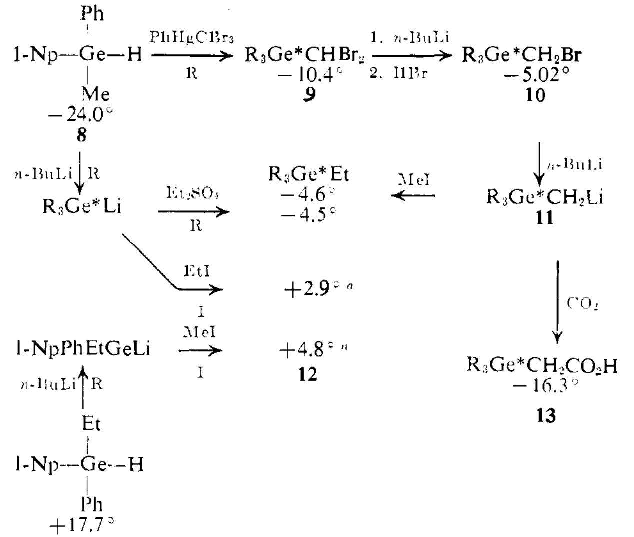
R_3Si^* = 1-naphthylphenylmethylsilyl
R = retention; I = inversion

Reaction with excess methyl iodide gave 1-naphthylphenylmethylethylsilane (**5**) contaminated with some 1-naphthylphenyldimethylsilane which presumably resulted from hydrolysis of **4** or from its metalation of the solvent. Taking into account dilution of the active material by the dimethylsilane, the proportion of which was determined by nuclear magnetic resonance spectroscopy (nmr) and by gas–liquid partition chromatography (glpc), the specific rotation of the R_3Si^*Et was found in two experiments to be +6.03 and +6.18°. Comparison of these values with the value of −6.1° reported by Sommer[7] for R_3Si^*Et from the coupling of ethyllithium with (−)-R_3Si^*Cl, a reaction which is considered to occur with essentially 100% inversion of configuration, indicates that dibromocarbene has inserted into the SiH bond with close to 100% retention of configuration. This is in agreement with Sommer's conclusions based on the assignment of inversion of configuration to the coupling of dibromomethyllithium with R_3Si^*Cl.[5] Based on the specific rotations of +8.7 and +9.15° found for the initially isolated and optically pure samples, respectively, of monobromide **3**, a stereospecificity for the carbene insertion of not less than 95% is indicated. Additionally, since bromide **3** was virtually optically pure and since the subsequent exchange and coupling reactions to give R_3Si^*Et did not involve the asymmetric center, the above experiments confirm Sommer's suggestion that the coupling of ethyllithium with R_3Si^*Cl[7] occurs with essentially complete inversion of configuration.

When $R_3Si^*CH_2Li$ was carbonated, the acid $R_3Si^*CH_2COOH$ (**6**), $[\alpha]_D$ +13.0°, was obtained. Treatment of this with diazoethane yielded its ethyl ester, **7**, as an oil, with $[\alpha]_D$ +4.65°. This same enantiomer, with almost the same specific rotation, was obtained directly from (+)-R_3Si^*H by its treatment with excess ethyl diazoacetate in the presence of cuprous chloride, indicating that insertion of carbethoxycarbene into the SiH bond occurs with close to 100% retention of configuration.

A similar sequence of reactions, outlined in Scheme II, was carried out with 1-naphthylphenylmethylgermane (**8**) which showed that dibromocarbene had inserted into the GeH bond stereospecifically with virtually complete retention of configuration. Thus, starting from (−)-R_3Ge^*H, $[\alpha]_D$ −24° (90% optical purity), reaction with dibromocarbene gave (−)-$R_3Ge^*CHBr_2$ (**9**), $[\alpha]_D$ −10.4°. Halogen–metal exchange, followed by protonation with HBr gave (−)-$R_3Ge^*CH_2Br$ (**10**), $[\alpha]_D$ −5.02°, which was crystallized to constant melting point and optical rotation and hence is probably optically pure. Conversion to the ethyl compound *via* coupling of the organolithium reagent **11** with methyl iodide gave a 90% yield of material, $[\alpha]_D$ −4.13°, shown by nmr and glpc to contain 90% R_3Ge^*Et (**12**) and 10% 1-naphthylphenyldimethylgermane. The calculated specific rotation of the pure ethyl compound is thus −4.6°. In addition, carbonation of the organolithium reagent gave the acid $R_3Ge^*CH_2CO_2H$ (**13**) $[\alpha]_D$ −16.3°. There is now a considerable body of evidence that

Scheme II



R_3Ge^* = 1-naphthylphenylmethylgermyl
R = retention; I = inversion
[a] Reference 12.

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(6) D. Seyferth and J. M. Burlitch, *J. Amer. Chem. Soc.*, **85**, 2667 (1963); D. Seyferth, J. M. Burlitch, D. Dertouzous, and H. D. Simmons, Jr., *J. Organometal. Chem.*, 7, 405 (1967).

(7) L. H. Sommer, W. D. Korte, and P. G. Rodewald, *J. Amer. Chem. Soc.*, **89**, 862 (1967).

chiral organosilicon and organogermanium compounds with the same absolute configuration have, in accord with Brewster's rules,[8] the same sign of rotation.[9–12] Thus the finding that the series of compounds described above, R_3M^*R' (R' = H, $CHBr_2$, CH_2Br, CH_2CH_3, CH_2CO_2H) derived from (+)-1-NpPhMeSiH and (−)-1-NpPhMeGeH have opposite signs of rotation (dextrorotatory for silicon, levorotatory for germanium) constitutes sound evidence that the dibromocarbene insertion into the GeH bond has occurred with a high degree of retention of configuration, the same stereochemistry as observed with SiH. Also, since bromide **10** was crystallized to a maximum optical rotation and since its subsequent conversion to R_3Ge^*Et did not involve the asymmetric center, $-4.6°$ probably represents a near maximum specific rotation for this compound. This receives additional support from the recent finding in these laboratories that the coupling of R_3Ge^*Li (from (−)-R_3Ge^*H) with diethyl sulfate (with retention of configuration) gave the same enantiomer with $[\alpha]_D$ $-4.5°$[13] and the value also compares favorably with the maximum rotation of 4.8° found for the coupling product of 1-naphthylphenylethylgermyllithium with methyl iodide.[12]

The above work demonstrates that (−)-R_3Ge^*H and (−)-R_3Ge^*Et have the same configuration. It follows, since the coupling of 1-naphthylphenylmethylgermyllithium (from (−)-R_3Ge^*H) with ethyl iodide (to give (+)-R_3Ge^*Et) has been shown to involve inversion of configuration,[11] that the conversion of R_3Ge^*H to R_3Ge^*Li must involve retention of configuration, as suggested previously.[10]

The third chiral methyllithium reagent was prepared by the metalation of 1-naphthylphenylmethylbenzylsilane (**14**), $[\alpha]_D$ $-6.8°$, a compound of known absolute configuration,[9] using the *n*-butyllithium–tetramethylethylenediamine (TMEDA) complex.[14] Deuterolysis of the organolithium reagent, **15**, gave α-deuteriobenzylsilane (**16**), $[\alpha]_D$ $-7.2°$, which was shown by nmr spectroscopy to be over 90% deuterated. The mixture melting point of this with starting benzylsilane was undepressed suggesting that the stereochemistry at silicon had not been affected by the metalation.

Carbonation of **15** gave two diastereomeric carboxylic acids **17a** and **17b** which were distinguishable by their nmr spectra in carbon tetrachloride solution, **a** having a one-proton benzal signal at 4.27 ppm and a three-proton silicon methyl signal at 0.63 ppm while **b** showed the corresponding signals at 4.20 and 0.68 ppm. The relative proportion of these diastereomers depended quite markedly on the conditions used for the carbonation. Thus when the clear, deep red ether solution of **15** at room temperature was treated with crushed Dry Ice the resulting product was a 30:70 mixture of **a** and **b**, respectively. This mixture, after purification by chromatography, had a specific rotation of $-7.1°$ (average of two runs). At $-78°$ a ratio of **a**:**b** of 44:56 was usually obtained except under conditions where an orange precipitate, presumably the $R_3Si^*CHPhLi$–TMEDA complex, was formed, in which case the ratio of **17a** to **17b** was 87:13 or 86:14, a dramatic change in proportions. The 87:13 diastereomeric mixture had a specific rotation of $+18.6°$. Based on the rotations found for the different proportions of **a** and **b** it can be calculated that the pure compounds would have specific rotations of about $+24.5$ and $-20.8°$, respectively. However, these values cannot be confirmed at the present time since it has not been possible to crystallize or otherwise separate the diastereomers.

Rearrangements of Silylacetic Acids. When 1-naphthylphenylmethylsilylacetic acid was heated, a mixture of products consisting of acetoxysilane (**18**), the silylacetoxysilane (**19**), and acetic acid was observed. The proportions of these products depended on the experimental conditions. From one run involving thermolysis of a neat sample of acid in a sealed, acid-washed Pyrex tube at 250° for 50 min, the 60% yield of acetoxysilane isolated had $[\alpha]_D$ $+2.9°$. Since optically pure acetoxysilane has $[\alpha]_D$ 17.7°[15] this corresponds to a process involving 17% net retention of configuration at silicon. However it is apparent that there are both unimolecular and bimolecular processes occurring and it has been found that the reaction of silylacetic acid with acetoxysilane to form silylacetoxysilane (eq 2 below) is at least as rapid as the direct formation of acetoxysilane from the acid. The implications of the above result are therefore not clear since the observed low net retention of configuration can arise both from intramolecular rearrangement involving retention (eq 1) and additionally from two subsequent steps (eq 2 and 3) which may involve inversion processes (in general, displacements on acyloxysilanes have been found to occur with inversion of configuration[15,16]).

$$\underset{\textbf{6}}{R_3Si^*CH_2CO_2H} \xrightarrow{\Delta} \underset{\textbf{18}}{R_3Si^*OCOCH_3} + \underset{\textbf{19}}{R_3Si^*OCOCH_2Si^*R_3} + CH_3CO_2H$$

$$R_3Si^*CH_2CO_2H \xrightarrow{R} R_3Si^*OCOCH_3 \qquad (1)$$

$$R_3Si^*CH_2CO_2H + R_3Si^*OCOCH_3 \xrightarrow{I} R_3Si^*OCOCH_2Si^*R_3 + CH_3CO_2H \qquad (2)$$

$$CH_3CO_2H + R_3Si^*OCOCH_2Si^*R_3 \xrightarrow{I} R_3Si^*OCOCH_3 + R_3Si^*CH_2CO_2H \qquad (3)$$

Similar processes have been found to occur in the thermolysis of (1-naphthylphenylmethylsilyl)phenylacetic acid but in this case the rearrangement goes to completion in a much shorter time and the bimolecular product is only detectable as a transient intermediate. When a neat sample of acids **17** (30% **a**, 70% **b**, $[\alpha]_D$ $-6.4°$) was heated under nitrogen at 165° for 40 min a quantitative yield of phenylacetoxy-1-naphthylphenylmethylsilane (**20**), with $[\alpha]_D$ $-2.0°$, was obtained. This represents about 20% net retention of configuration so that the results obtained are closely analogous to

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(8) J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959).

(9) A. G. Brook and W. W. Limburg, *ibid.*, **85**, 832 (1963).

(10) A. G. Brook and G. J. D. Peddle, *ibid.*, **85**, 2338 (1963).

(11) C. Eaborn, R. E. E. Hill, and P. Simpson, *J. Organometal. Chem.*, **15**, P1 (1968).

(12) C. Eaborn, R. E. E. Hill, P. Simpson, A. G. Brook, and D. M. MacRae, *ibid.*, **15**, 241 (1968).

(13) We are indebted to D. M. MacRae for this result.

(14) G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964).

(15) L. H. Sommer, G. A. Parker, and C. L. Frye, *J. Amer. Chem. Soc.*, **86**, 3280 (1964).

(16) L. H. Sommer, "Stereochemistry Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965, Chapter 3.

those obtained in the thermolysis of the silylacetic acid **6**.

When a solution of the silylphenylacetic acid in ether or tetrahydrofuran was treated with triethylamine quantitative isomerization to phenylacetoxysilane occurred. Kinetic studies have shown that the reaction involves both a direct unimolecular rearrangement (eq 4) and a reaction involving a bimolecular equilibrium (eq 5).

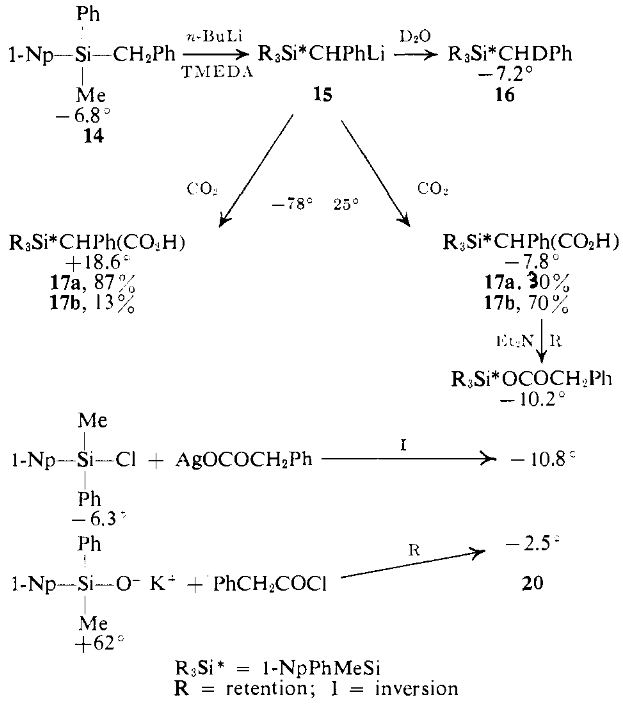
$$R_3Si^*CHPh(CO_2H) \xrightarrow{Et_3N} R_3Si^*OCOCH_2Ph \qquad (4)$$

$$R_3Si^*CHPhCO_2H + R_3Si^*OCOCH_2Ph \overset{Et_3N}{\rightleftarrows} R_3Si^*CHPhCO_2Si^*R_3 + PhCH_2CO_2H \qquad (5)$$

The extent to which the bimolecular reaction occurs can be minimized if the acid is slowly added to an excess of the amine in a large volume of ether. When acid **17** (30% **a**, 70% **b**, [α]D −6.4°) was rearranged under these conditions the resulting oil, phenylacetoxy-1-naphthylphenylmethylsilane (**20**), had [α]D −9.7 and −10.2° for two different runs. When the same rearrangement was carried out under conditions where the bimolecular equilibrium predominated (high acid concentration and lower base concentration in tetrahydrofuran solvent) the resulting phenylacetoxysilane had a specific rotation of only −4.7°.

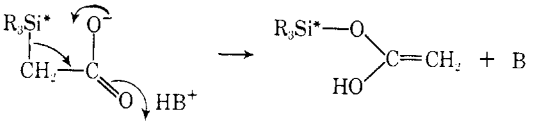
All known acyloxysilanes with the same relative configuration as (−)-R_3Si^*H are levorotatory,[17] as expected from Brewster's rules. Since the (−)-phenylacetoxysilane isolated is derived from the acids **17a** and **17b** which have the (−)-R_3Si^*H configuration it follows that the rearrangement of acid **17** has occurred with retention of configuration as is shown in Scheme III. This assignment is confirmed by comparison with authentic (−)-phenylacetoxysilane, prepared by an alternate route of known stereochemistry.

Scheme III



R_3Si^* = 1-NpPhMeSi
R = retention; I = inversion

The attempt to prepare phenylacetoxysilane **20** from the reaction of (+)-R_3Si^*OK[18] with phenylacetyl chloride was relatively unsuccessful since the yield of **20** was only 50%, which after purification by chromatography on silica gel had a specific rotation of only −2.5°. A more successful route to **20** was the coupling of (−)-R_3Si^*Cl with silver phenylacetate, a reaction involving inversion of configuration, which gave phenylacetoxysilane, [α]D −10.8°, in high yield. This material is probably of high optical purity judged from our experience of the coupling of silver acetate with R_3Si^*Cl. Hence the rotations of −9.7 and −10.2° observed for the phenylacetoxysilane from rearrangement of the acid suggest that the base-catalyzed rearrangement occurs with nearly complete retention of configuration, as would be expected for an intramolecular process involving a four-centered transition state.



A similar mechanism has been proposed to account for the observed retention stereochemistry in the unimolecular thermal rearrangement of β-ketosilanes.[19]

The work described above has clearly indicated the utility of the chiral silyl- and germylmethyllithium reagents for the synthesis of a variety of organometalloidal compounds of high optical purity and suggests that they will prove to be valuable synthetic intermediates and stereochemical probes for many other studies in organometalloid systems.

Experimental Section

All reactions involving organometallic reagents were carried out under an atmosphere of nitrogen using solvents dried over lithium aluminum hydride or sodium. The nmr spectra were measured on a Varian A-60 instrument and the infrared spectra were recorded on a Perkin-Elmer 237B instrument. Specific rotations were measured manually in a 1-dm cell. Gas chromatographic analyses were carried out with a 20 ft × 3/8 in. column of 20% SE30 (silicone gum) on Chromosorb W using a Varian Series 200 dual column instrument.

Synthesis of (+)-$R_3Si^*CHBr_2$. A mixture of 15 g (0.0605 mol) of 1-naphthylphenylmethylsilane, (+)-R_3Si^*H,[20] [α]D +34.5° (*c* 11.86, cyclohexane), and 34.5 g (0.065 mol) of tribromomethylphenylmercury[21] in 250 ml of dry benzene was heated at 68° for 3 days when, since an infrared spectrum of the crude reaction mixture still showed the presence of SiH, a further 12 g (total 0.0875 mol) of mercurial was added. The mixture was stilled at 68° for a further 2 days. Work-up by filtration gave 28 g (90%) of phenylmercuric bromide and 28 g of crude product which after chromatography through silica gel to remove phenylmercuric bromide gave 16.5 g (65%) of an oil. Further chromatography on neutral alumina using *n*-hexane containing 10% carbon tetrachloride as eluent produced a total of 11.5 g (45%) of pure material: $[\alpha]^{25}D$ +18.5° (*c* 14.1, cyclohexane) (lit.[5] [α]D 14.3°, solvent and concentration unspecified); nmr (CCl_4) δ 0.98 (s, 3 H), 5.76 (s, 1 H), 7.2–8.0 ppm (m, 12 H). Repetition of the experiment yielded 48% of material with $[\alpha]^{25}D$ +18.6°.

Anal. Calcd for $C_{18}H_{16}Br_2Si$: C, 51.46; H, 3.84. Found: C, 51.55; H, 3.84.

Synthesis of (+)-$R_3Si^*CH_2Br$. A solution of 3.10 g (0.00738 mol) of (+)-$R_3Si^*CHBr_2$, $[\alpha]^{24}D$ +18.5° (*c* 14.1, cyclohexane), in 250 ml of Et_2O was treated at −78° with 5 ml (0.008 mol) of 1.6 *M*

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[17] Reference 16, p 44.

[18] L. H. Sommer, *Angew. Chem., Int. Ed. Engl.*, 1, 143 (1962).

[19] A. G. Brook, D. M. MacRae, and W. W. Limburg, *J. Amer. Chem. Soc.*, **89**, 5493 (1967).

[20] L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *ibid.*, **86**, 3271 (1964).

[21] D. Seyferth and R. L. Lambert, Jr., *J. Organometal. Chem.*, **16**, 21 (1969).

n-butyllithium solution. After 8 min at −78° anhydrous hydrogen bromide was slowly passed into the solution for 10 min. Aqueous work-up gave 2.1 g of an oil (84%). Chromatography on silica gel gave 1.95 g (78%) of 1-naphthylphenylmethylbromomethylsilane, mp 59.5–62°, $[\alpha]^{23}\mathrm{D}$ +8.7° (*c* 11.5, cyclohexane). Recrystallization raised the mp to 63.5–64.5°, and constant $[\alpha]^{23}\mathrm{D}$ 9.15° (*c* 10.4, cyclohexane); nmr (CCl_4) δ 0.85 (s, 3 H), 3.00 (s, 2 H), 7.2–8 ppm (m, 12 H).

Anal. Calcd for $C_{18}H_{17}SiBr$: C, 63.34; H, 5.02. Found: C, 63.35; H, 5.09.

Repetition of the experiment gave 72% of chromatographed material, with $[\alpha]^{23}\mathrm{D}$ +8.83°, raised by recrystallization to $[\alpha]^{23}\mathrm{D}$ +9.11° (*c* 10.2, cyclohexane).

Preparation of R_3Si^*Et from $R_3Si^*CH_2Li$ and Methyl Iodide. To 0.56 g (0.00164 mol) of 1-NpPhMeSiCH$_2$Br, $[\alpha]^{23}\mathrm{D}$ +9.15° (*c* 10.4, cyclohexane), dissolved in 50 ml of ether and cooled to −78° was added 1.12 ml (0.0018 mol) of 1.6 *M n*-butyllithium in *n*-hexane; the solution turned pale yellow. After 30 min, 0.912 g of methyl iodide was added. The solution was stirred at −78° for 35 min and then was slowly allowed to warm to room temperature. The yellow color completely disappeared. Work-up gave 0.442 g of an oil shown to be 80% 1-naphthylphenylmethylethylsilane (1-NpPhMeEtSi) and 20% 1-naphthylphenyldimethylsilane (1-NpPhMe$_2$Si). This oil had $[\alpha]^{23}\mathrm{D}$ +4.82° (*c* 9.33 *n*-pentane). Correcting for the purity of this material, the specific rotation of the R_3Si^*Et is +6.03° (lit.[7] $[\alpha]\mathrm{D}$ −6.1° (*c* 8.8, pentane) for the enantiomer).

The experiment was repeated using larger quantities and glpc to investigate the mixture of products. Thus 1.5 g of (+)-$R_3Si^*CH_2Br$, $[\alpha]^{23}\mathrm{D}$ +9.11° (*c* 10.2, cyclohexane), was treated as above except that 3 ml of methyl iodide was used to derivatize the reagent. Work-up yielded 1.21 g (100%) of product. Distillation by Kugelrohr gave 0.92 g (76%) of impure R_3Si^*Et, bp 170° (0.35 mm), $n^{24}\mathrm{D}$ 1.6206 (lit.[7] $n^{27}\mathrm{D}$ 1.6183), $[\alpha]^{23}\mathrm{D}$ +5.05° (*c* 9.94, pentane), shown by glpc to contain 18.5% of 1-NpPhSiMe$_2$; hence the calculated $[\alpha]\mathrm{D}$ of the (+)-R_3Si^*Et is 6.18°.

Attempts to separate the 1-NpPhMeEtSi from the 1-NpPhMe$_2$Si by preparative glpc failed due to the nearness of the retention times of the two materials (when larger quantities of material were placed on the column, the two peaks seriously overlapped one another).

Synthesis of (+)-$R_3Si^*CH_2COOH$. A solution of 2.5 g (0.00733 mol) of (+)-$R_3Si^*CH_2Br$, $[\alpha]\mathrm{D}$ +9.11° (*c* 10.2, cyclohexane), in 150 ml of ether was treated with 4.9 ml of 1.6 *M n*-butyllithium (0.0078 mol) at −78°. After 0.5 hr the solution was carbonated by transferring the organolithium reagent (still at −78°) with a hypodermic syringe to powdered Dry Ice covered by ether in a loosely capped vessel. After normal work-up in the cold, 2.5 g (120%) of an oil was obtained. Crystallization from cyclohexane–*n*-hexane gave 1.8 g (80%) of 1-naphthylphenylmethylsilylacetic acid, mp 119–121°, $[\alpha]^{24}\mathrm{D}$ 12.6° (*c* 10.33, chloroform). Recrystallization raised the mp to 121–121.5°, $[\alpha]^{26}\mathrm{D}$ +13.0° (*c* 10.78, chloroform); nmr δ 0.83 (s, 3 H), 2.59 (s, 2 H), 7.2–8 ppm (m, 12 H); ir (CCl_4) 3.0–4.0 (broad), 5.76 (weak), 5.91 (strong, COOH), 7.0, 9.0 (Si–Ph), 7.97 μ (Si–Me).

Anal. Calcd for $C_{19}H_{18}SiO_2$: C, 74.47; H, 5.92. Found: C, 74.46; H, 5.88.

Preparation of $R_3Si^*CH_2COOEt$. A. Esterification of R_3Si^*-CH_2CO_2H. Diazoethane was prepared by the rapid addition of a solution of 1.5 g (0.010 mol) of ethyl-*N*-nitroso-*N*-ethylurethane in 10 ml of ether to a solution of 20 ml of ether and 20 ml of *n*-propyl alcohol containing 1.5 g of potassium hydroxide. The diazoethane was distilled with an additional 50 ml of ether using a water bath at 50°.

The distillate was added to a solution of 1.00 g (0.00326 mol) of (+)-$R_3Si^*CH_2COOH$, $[\alpha]^{22}\mathrm{D}$ +13.0° (*c* 10.78, chloroform), in 100 ml of ether, cooled with an ice–water bath, until the yellow-orange color of the diazoalkane persisted in the reaction flask. Removal of the solvents gave 1.06 g (95%) of an oil, $[\alpha]^{23}\mathrm{D}$ +4.56° (*c* 9.88, cyclohexane). Distillation of the oil (Kugelrohr, bp 200° (0.15 mm)) gave 0.98 g (90%) of an oil, $n^{21}\mathrm{D}$ 1.6051; $[\alpha]^{24}\mathrm{D}$ +4.65° (*c* 10.75, cyclohexane); nmr ($CDCl_3$) δ 0.82 (s, 3 H, Si–CH_3), 0.91 (t, J = 7 cps, 3 H, CH_3CH_2–O), 2.57 (s, 2 H, Si–CH_2), 3.89 (q, J = 7 cps, 2 H, CH_3CH_2–O), and 7.15–8.0 ppm (m, 12 H, aromatic); ir (CCl_4) 5.81 μ (C=O).

Anal. Calcd for $C_{21}H_{22}O_2Si$: C, 75.41; H, 6.63. Found: C, 75.44; H, 6.52.

B. From R_3Si^*H + Carbethoxycarbene. To 5.0 g (0.0202 mol) of (+)-R_3Si^*H, $[\alpha]^{24}\mathrm{D}$ +34.5° (*c* 11.87, cyclohexane), in 150 ml of dry benzene was added 0.25 g of cuprous chloride. To this mixture 12.0 g of ethyl diazoacetate was added slowly over 1.25 hr. The mixture was left stirring for 1 hr after the addition was completed. After removal of solvents, distillation gave 2.9 g of a mixture of diethyl maleate and diethyl fumarate, 2.5 g (50%) of (+)-R_3Si^*H, and 1.6 g (24%) of crude ester, bp 215° (0.3 mm), $[\alpha]^{25}\mathrm{D}$ 3.87° (*c* 31.04, cyclohexane). Chromatography on silica gel with carbon tetrachloride followed by benzene as eluents gave 1.4 g (21%) of a clear oil having $[\alpha]\mathrm{D}$ +4.44° (*c* 13.51, cyclohexane), with nmr and infrared spectra identical with those of the material prepared by the alternate route A.

Preparation of (−)-$R_3Ge^*CHBr_2$. A mixture of 4.4 g (0.015 mol) of (−)-R_3Ge^*H, $[\alpha]^{25}\mathrm{D}$ −24.0° (*c* 19.2, cyclohexane), and 8.75 g (0.0165 mol) of tribromomethylphenylmercury in 100 ml of dry benzene was heated at reflux for 2 hr. Filtration of the cooled suspension gave 5.5 g (93%) of phenylmercuric bromide. Removal of solvent followed by chromatography of the oil from silica gel using carbon tetrachloride as eluent gave 4.6 g (66%) of an oil, $[\alpha]^{26}\mathrm{D}$ −9.82° (*c* 16.3, cyclohexane). Further chromatography gave pure 1-naphthylphenylmethyl(dibromomethyl)germane, $[\alpha]^{28}\mathrm{D}$ −10.4° (*c* 11.07, cyclohexane); nmr ($CDCl_3$) δ 1.09 (s, 3 H, CH_3–Ge), 5.85 (s, 1 H, $CHBr_2$) and 7.1–8.05 ppm (m, 12 H, aromatic).

Anal. Calcd for $C_{18}H_{16}GeBr_2$: C, 46.52; H, 3.47. Found: C, 46.82; H, 3.53.

An additional experiment gave 62% of (−)-$R_3Ge^*CHBr_2$, $[\alpha]\mathrm{D}$ −10.2° (*c* 17.7, cyclohexane).

Preparation of (−)-$R_3Ge^*CH_2Br$. A solution of 1.68 g (0.00362 mol) of (−)-$R_3Ge^*CHBr_2$, $[\alpha]^{26}\mathrm{D}$ −10.4° (*c* 11.07, cyclohexane), in 75 ml of dry ether was cooled to −78° and 2.5 ml (0.0040 mol) of 1.6 *M n*-butyllithium in hexane was added. After 5 min, anhydrous hydrogen bromide gas was bubbled through the solution. Aqueous work-up gave 1.31 g of an oil.

Chromatography of the oil on silica gel using carbon tetrachloride as eluent gave a fraction which contained 0.30 g (22%) of (−)-$R_3Ge^*CH_2Br$. Recrystallization gave 0.20 g (14%) of the desired product, mp 50–53.5°. Some naphthalene was also obtained. This synthesis was repeated using a lower temperature, as follows.

A solution of (−)-$R_3Ge^*CHBr_2$ (4.04 g, 0.0087 mol), $[\alpha]^{23}\mathrm{D}$ −10.2° (*c* 17.7, cyclohexane), in 240 ml of ether–tetrahydrofuran (1:1 by volume) was cooled to −120° in a methylcyclohexane–liquid nitrogen slush and 6.0 ml (0.0096 mol) of *n*-butyllithium was added quickly. The solution turned yellow instantly and the color deepened over 10 min. Hydrogen bromide gas was bubbled through the solution for 2 min. The cooling bath was removed and the passage of HBr was continued until all the color disappeared. Work-up gave 3.23 g (97%) of white solid, mp 42–47°, $[\alpha]^{25}\mathrm{D}$ −4.32° (*c* 22.00, cyclohexane).

Recrystallization of the sample from *n*-pentane and *n*-hexane gave 2.65 g (79%) of 1-naphthylphenylmethyl(bromomethyl)germane, mp 59.5–60.5°, $[\alpha]^{26}\mathrm{D}$ −5.02° (*c* 20.98, cyclohexane); nmr ($CDCl_3$) δ 0.94 (s, 3 H, Ge–CH_3), 3.17 (s, 2 H, CH_2) 7.2–8.0 ppm (m, 12 H, aromatic).

Anal. Calcd for $C_{18}H_{17}GeBr$: C, 56.06; H, 4.44. Found: C, 56.19; H, 4.51.

Preparation of (−)-$R_3Ge^*CH_2CH_3$. A. From $R_3Ge^*CH_2Li$ + Methyl Iodide. To 0.40 g (0.0010 mol) of (−)-$R_3Ge^*CH_2Br$, $[\alpha]\mathrm{D}$ −5.02° (*c* 20.98, cyclohexane), in 10 ml of ether at room temperature was added 0.80 ml (0.0013 mol) of *n*-butyllithium. After stirring at room temperature for 5 min, 1 ml of dry methyl iodide was added. The solution was stirred for 0.5 hr. Work-up gave 0.30 g (90%) of product after distillation (bp 205° (0.05 mm Kugelrohr)), $[\alpha]^{24}\mathrm{D}$ −4.13° (*c* 10.18, cyclohexane) (lit.[12] $[\alpha]^{26}\mathrm{D}$ 4.8° (*c* 5.5, cyclohexane)). An nmr spectrum of this material showed it to consist of 90% 1-NpPhMeGeEt and 10% 1-NpPhGeMe$_2$. Use of glpc to analyze this product showed 89% 1-NpPhMeGeEt and 11% 1-NpPhGeMe$_2$, with a sample size of 5 μl. Pure R_3Ge^*Et therefore has $[\alpha]\mathrm{D}$ −4.60°.

B. From R_3Ge^*Li + Diethyl Sulfate. A solution of 1.04 g (0.0036 mol) of R_3Ge^*H, $[\alpha]\mathrm{D}$ −24.0° (*c* 19.2, cyclohexane), in 50 ml of dry ether at room temperature was heated with 2.8 ml (0.0044 mol) of *n*-butyllithium in hexane. A yellow-brown solution was obtained. After 1 hr 1 ml of diethyl sulfate was added. The color was discharged instantly and a white precipitate formed. Aqueous work-up gave an oil which was distilled twice (190° (0.05 mm Kugelrohr)) to give pure 1-naphthylphenylmethylethylgermane, $[\alpha]^{24}\mathrm{D}$ −4.5° (*c* 13.52, cyclohexane).

Preparation of (−)-$R_3Ge^*CH_2COOH$. To 0.60 g (0.0016 mol) of (−)-$R_3Ge^*CH_2Br$, $[\alpha]^{26}\mathrm{D}$ −5.02° (*c* 20.98, cyclohexane), in 15 ml of ether at 20° was added 1.2 ml (0.0019 mol) of 1.6 *M n*-butyllithium in *n*-hexane. After 5 min, the mixture was removed from the flask with a syringe and injected into a flask containing solid carbon dioxide and dry ether. Work-up gave 0.52 g (96%) of crude product as an oil. Crystallization from *n*-hexane–cyclohexane gave 0.34 g (63%) of 1-naphthylphenylmethylgermylacetic acid, mp 116.5°–118.5°, $[\alpha]^{24}\mathrm{D}$ −16.3° (*c* 18.2, chloroform); nmr ($\mathrm{CDCl_3}$) δ 0.93 (s, 3 H, Ge–$\mathrm{CH_3}$), 2.57 (s, 2 H, $\mathrm{CH_2}$–Ge), 7.2–8.0 (m, 12 H, aromatic), 10.31 ppm (s, 1 H, COOH); ir ($\mathrm{CCl_4}$) 5.93 (C=O), 6.98 and 9.15 μ (Ge–aryl).

Anal. Calcd for $\mathrm{C_{19}H_{18}GeO_2}$: C, 65.08; H, 5.17. Found: C, 65.11; H, 5.21.

Preparation of $\mathrm{R_3Si{*}CHPhLi}$ and Its Deuterolysis. A solution of 0.34 g (0.0010 mol) of (−)-$\mathrm{R_3Si{*}CH_2Ph}$, $[\alpha]\mathrm{D}$ −6.8°, in 10 ml of dry ether containing 0.14 g (0.0012 mol) of TMEDA was treated with 0.75 ml (0.0012 mol) of *n*-butyllithium solution. The solution turned red within minutes. After 1.5 hr at room temperature, 3 ml of $\mathrm{D_2O}$ was added to the clear red solution. Work-up gave an oil which was shown by nmr to be 90% deuterated, the ratio of the PhC*H*D signal (a broad structureless band) to the Si–$\mathrm{CH_3}$ singlet being 1.1:3. Crystallization from methanol gave 0.24 g (71%) of pure product, mp 69–70.5°, $[\alpha]^{24}\mathrm{D}$ −7.2° (*c* 11.03, cyclohexane). The mixture melting point of this material with the starting benzylsilane (mp 69–70.5°) was undepressed.

Preparation of $\mathrm{R_3Si{*}CHPhCO_2H}$. A. Carbonation of the Precipitated Reagent at −78°. A solution of 1.52 g (0.0045 mol) of (−)-$\mathrm{R_3Si{*}CH_2Ph}$, $[\alpha]\mathrm{D}$ −6.6° (*c* 10.8°, cyclohexane), in 25 ml of dry ether at room temperature was treated with 0.78 g (0.0067 mol) of TMEDA followed by 4.2 ml (0.0067 mol) of *n*-butyllithium solution. A clear red solution resulted. On standing for 2.5 hr at room temperature the solution had formed an orange precipitate. It was cooled to −78° and was treated with 5 g of crushed Dry Ice. The color disappeared within seconds and when the solid carbon dioxide had sublimed the reaction was worked up with dilute hydrochloric acid to give 1.68 g (98%) of crude oil as an 87:13 mixture of diastereomers **17a** and **17b**, respectively, $[\alpha]\mathrm{D}$ +18.1° (*c* 10.5, chloroform). Chromatography on silica gel gave a small amount of nonpolar material on elution with benzene and the same mixture of acids, a glass having $[\alpha]^{26}\mathrm{D}$ +18.9°, was obtained on elution with methylene chloride. A final purification by chromatography gave the pure acids (still an 87:13 ratio of diastereomers), $[\alpha]^{23}\mathrm{D}$ +18.6° (*c* 9.17, chloroform); nmr ($\mathrm{CCl_4}$) δ 0.68, 0.63 (0.39 and 2.61 H, respectively, $\mathrm{SiCH_3}$), 4.27, 4.20 (0.87 and 0.13 H, respectively, PhC*H*), 7.2–7.9 (m, 17 H, aromatic), and 10.0 ppm (1 H, broad, $\mathrm{CO_2}$*H*); ir ($\mathrm{CCl_4}$) 3–4 (broad), 5.75 (weak), 5.92 μ (strong).

Anal. Calcd for $\mathrm{C_{25}H_{22}O_2Si}$: C, 78.49; H, 5.79. Found: C, 78.73; H, 5.87. Attempts to crystallize this material from a wide variety of solvents gave only oils.

B. Carbonation of the Reagent in Solution at Room Temperature. To 6.76 g (0.02 mol) of $\mathrm{R_3Si{*}CH_2Ph}$ $[\alpha]\mathrm{D}$ −6.8°, in 140 ml of ether was added 2.56 g (0.022 mol) of TMEDA, followed by 14.4 ml (0.023 mol) of *n*-butyllithium. The clear red solution was carbonated after 1.25 hr at room temperature. Work-up as above gave crude acid as a 30:70 mixture of **17a** and **17b**, respectively. Chromatography on silica gel, eluting first with 1:1 benzene–carbon tetrachloride, then with 20% ether in benzene, gave 4.45 g (59%) of pure acid, as a glass, $[\alpha]^{24}\mathrm{D}$ −7.8°, in the first fraction. This material was shown by nmr to be a 30:70 mixture of diastereomers **a** and **b**.

Repetition of the experiment on a slightly smaller scale gave the same ratio of diastereomers having $[\alpha]\mathrm{D}$ −6.4°. Attempts to crystallize this material from a variety of solvents were unsuccessful.

The Thermolysis of $\mathrm{R_3Si{*}CH_2CO_2H}$. A 0.30-g sample of 1-naphthylphenylmethylsilylacetic acid, $[\alpha]^{24}\mathrm{D}$ +13.0°, was placed in an acid-washed Pyrex tube under nitrogen. After heating at 250° for 50 min ir and nmr spectroscopy showed mainly acetoxysilane ($\mathrm{R_3Si{*}OCOCH_3}$) to be present. This product was distilled (Kugelrohr, 230° (0.5 mm)) to give 0.18 g (60%) of acetoxysilane, $[\alpha]^{24}\mathrm{D}$ +2.9° (*c* 6.95, hexane) (lit.[15] $[\alpha]\mathrm{D}$ 17.7°).

The Thermolysis of $\mathrm{R_3Si{*}CHPh(CO_2H)}$. Preliminary experiments which were carried out by heating neat samples of the acid at 165° in nmr tubes showed that the rearrangement to phenylacetoxy-1-naphthylphenylmethylsilane was quantitative and complete in about 35 min.

A sample of 0.126 g of (1-naphthylphenylmethylsilyl)phenylacetic acid, 30:70 ratio of diastereomers, $[\alpha]\mathrm{D}$ −6.4°, was placed in a tightly stoppered 1-ml volumetric flask under nitrogen. The flask was then immersed in a 165° oil bath for 50 min. The resulting oil was dissolved in cyclohexane and the specific rotation at 25° was found to be −0.4°.

Repetition of the experiment by heating a 0.204-g sample of acid for 41 min gave phenylacetoxysilane having $[\alpha]^{25}\mathrm{D}$ −2.0° (*c* 10.2, cyclohexane).

The Base-Catalyzed Rearrangement of $\mathrm{R_3Si{*}CHPh(CO_2H)}$. A. A solution of 1.15 g (0.003 mol) of (1-naphthylphenylmethylsilyl)phenylacetic acid (30:70 ratio of **a** and **b**, $[\alpha]\mathrm{D}$ −6.4°) in 50 ml of dry ether in an addition funnel was added to a well-stirred solution of 4.6 ml (3.33 g, 0.033 mol) of triethylamine in 200 ml of dry ether under nitrogen. The addition lasted 40 min after which the solution was stirred for a further 5 min. Removal of solvents at reduced pressure gave a thick oil, $[\alpha]^{23}\mathrm{D}$ −8.3°, shown by ir and nmr to consist mainly of phenylacetoxy-1-naphthylphenylmethylsilane along with minor amounts of 1-naphthylphenylmethylsilanol and triethylammonium phenylacetate. Rapid chromatography on a 1.25-in. diameter × 1.5-in. column of silica gel, eluting with 1:1 benzene–carbon tetrachloride, removed the impurities, giving pure phenylacetoxysilane, $[\alpha]^{24}\mathrm{D}$ −9.7° (*c* 9.75, cyclohexane).

Repetition of the experiment gave crude material, $[\alpha]^{24}\mathrm{D}$ −8.2°, which upon purification had $[\alpha]^{24}\mathrm{D}$ −10.2° (*c* 12.25, cyclohexane).

The optically active phenylacetoxysilane could not be crystallized under a variety of conditions. Its spectral properties were identical with those of the racemate described below.

B. A solution of 1.15 g (0.0030 mol) of (1-naphthylphenylmethylsilyl)phenylacetic acid (30% **a**, 70% **b**), $[\alpha]\mathrm{D}$ −6.4°, in 150 ml of dry tetrahydrofuran was treated with 46 μl (0.033 g, 0.00033 mol) of triethylamine. Upon stirring for 4.5 hr at room temperature the solvents were removed at reduced pressure to give the crude phenylacetoxy-1-naphthylphenylmethylsilane, $[\alpha]^{24}\mathrm{D}$ −3.1°. Purification as above gave $[\alpha]^{24}\mathrm{D}$ −4.7° (*c* 8.45, cyclohexane). This material crystallized from 5 ml of dry hexane on standing at −20° giving 0.37 g (32%) of racemic product, mp 80–85°. Recrystallization gave the pure racemate, mp 83–84.5° (see below).

Alternative Synthesis of (−)-$\mathrm{R_3Si{*}OCOCH_2Ph}$. A. From (+)-$\mathrm{R_3Si{*}OK}$ and Phenylacetyl Chloride. A solution of 2.31 g (0.00877 mol) of (−)-$\mathrm{R_3Si{*}OH}$, $[\alpha]^{23}\mathrm{D}$ −19.3° (*c* 14.2, diethyl ether), in 24 ml of dry xylene was stirred with 7.8 g (0.14 mol) of powdered potassium hydroxide for 18 hr at room temperature. The suspension was filtered under nitrogen and the resulting clear yellow solution had an observed rotation corresponding to $[\alpha]^{22}\mathrm{D}$ +62° for the $\mathrm{R_3Si{*}OK}$ (lit.[19] $[\alpha]\mathrm{D}$ 70°). Addition of 1.38 g (0.0090 mol) of phenylacetyl chloride resulted in an exothermic reaction and the formation of a precipitate of potassium chloride. Filtration, followed by removal of the xylene at 100° under high vacuum (Kugelrohr), gave an oil, judged by nmr to contain 56% of $\mathrm{R_3Si{*}OCOCH_2Ph}$, 44% of $\mathrm{R_3Si{*}OH}$, and about 50% of recovered phenylacetyl chloride. The phenylacetoxysilane was isolated by chromatography on silica gel, a total of 1.57 g (47%), $[\alpha]^{23}\mathrm{D}$ −2.5° (*c* 12.15, cyclohexane), being eluted with 3:1 benzene–carbon tetrachloride. This oil crystallized from cyclohexane–pentane to give 0.90 g (27%) of racemic phenylacetoxysilane, mp 83–85°.

B. From (−)-$\mathrm{R_3Si{*}Cl}$ and Silver Phenylacetate. To a solution of 1.60 g (0.00567 mol) of (−)-$\mathrm{R_3Si{*}Cl}$, $[\alpha]^{24}\mathrm{D}$ −6.4° (*c* 10.15, cyclohexane), in 50 ml of dry benzene was added 1.45 g (0.00597 mol) of silver phenylacetate (prepared from potassium phenylacetate and silver nitrate and dried at 115° under high vacuum for 1 hr). The suspension was stirred for 10 hr in the dark, then was filtered through Celite to give, following removal of the solvent, an oil, $[\alpha]^{24}\mathrm{D}$ −10.8° (*c* 7.88, cyclohexane), which was shown by spectroscopy to be $\mathrm{R_3Si{*}OCOCH_2Ph}$ along with a trace of $\mathrm{R_3Si{*}OH}$. The nmr and ir spectra of this material were identical with those of the crystalline racemate described below.

Preparation of Racemic $\mathrm{R_3Si{*}OCOCH_2Ph}$. The oil obtained from the chlorination of 1.24 g (0.0050 mol) of (±)-$\mathrm{R_3Si{*}H}$ was dissolved in 50 ml of dry benzene and then was stirred with 1.28 g (0.0053 mol) of silver phenylacetate for 15 hr at room temperature in the dark. Work-up as above gave a thick oil which readily crystallized from cyclohexane–pentane to give 1.68 g (88%) of racemic phenylacetoxy-1-naphthylphenylmethylsilane, mp 80–83°. Several recrystallizations from dry hexane gave the analytical sample: mp 84–85°; nmr ($\mathrm{CCl_4}$) δ 0.90 (s, 3 H, $\mathrm{SiCH_3}$), 3.57 (s, 2 H, $\mathrm{PhCH_2}$), 7.0–7.9 ppm (m, 17 H, aromatic); ir ($\mathrm{CCl_4}$) 5.80 μ (C=O).

Anal. Calcd for $\mathrm{C_{25}H_{22}O_2Si}$: C, 78.49; H, 5.79. Found: C, 78.61; H, 5.76.

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