Stereochemistry of Asymmetric Silicon. III. Carboxylate and Tosylate Leaving Groups[1]

BY L. H. SOMMER, G. A. PARKER, AND C. L. FRYE

Reactions of optically active α-naphthylphenylmethylsilanes, R₃Si*X, proceed with predominant *inversion* of configuration with lithium aluminum hydride, KOH(s), and methanol, when X is a carboxylate group. The tosylate leaving group is displaced from asymmetric silicon with *inversion* of configuration by silanolate anion. These studies rigorously demonstrate *inversion* of configuration as an important stereochemical path for R₃Si*X reactions, when X is a good leaving group whose conjugate acid has pK_a less than *ca.* 6. Relative configurations for reactants and products were established by chemical correlations of configuration.
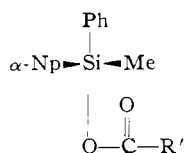
A previous paper[1] has dealt with the stereochemistry of reactions of R₃Si*X in which R₃Si*- is the α-naphthylphenylmethylsilyl group, α-NpPhMeSi*-, and X is an alkoxy or siloxy group. The latter are classed[2] as poor leaving groups—their conjugate acids have pK_a larger than *ca.* 10—and their reaction rates with strong nucleophiles are often relatively slow.[1] It was found that a *retention* stereochemistry obtains for the displacement of these groups in reactions with a number of strongly nucleophilic reagents in nonpolar aprotic solvents.

The change from alkoxy to carboxylate leaving groups greatly increases reaction rate with nucleophilic reagents. Carboxylate leaving groups have previously been classed as good leaving groups[2]—their conjugate acids have pK_a smaller than *ca.* 6—and it will be noted below that the change in leaving group from RO- to R'COO- engenders a significant change in stereochemistry. The tosylate leaving group is also a good leaving group and the stereochemistry of its displacement will be reported below.
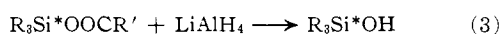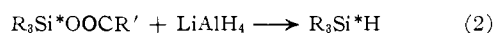
Syntheses and Chemical Correlations of Configurations.—Optically active R₃Si*OOCR' compounds were prepared from optically active potassium silanolate[1] and R'COCl. Since these reactions do not affect the asymmetric silicon center, and since (−)R₃Si*OK is known to have the (+)R₃Si*H configuration,[1,3] the R₃Si*OOCR' compounds prepared by general procedure 1 below all have the (+)R₃Si*H configuration.

$$(-)R_3Si^*OK + R'COCl \xrightarrow{\text{xylene}} R_3Si^*OOCR' \quad (1)$$
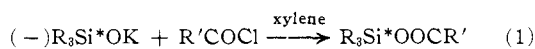
The acyloxysilanes prepared according to (1) are listed in Table I. In view of the known absolute configuration of (+)R₃Si*H,[3] the enantiomers given in Table I all have the absolute configuration

$$\alpha\text{-Np} \longrightarrow \overset{\text{Ph}}{\underset{\overset{|}{\underset{\overset{O}{O}—\overset{\overset{O}{\|}}{C}—R'}}{\text{Si}}} \longrightarrow \text{Me}$$

Reduction Reactions.—The reduction of R₃Si*OOCR' to R₃Si*H with lithium aluminum hydride, reaction 2, is accompanied by acyl-oxygen cleavage, reaction 3, to give R₃Si*OH as the isolated product.

$$R_3Si^*OOCR' + LiAlH_4 \longrightarrow R_3Si^*H \quad (2)$$

$$R_3Si^*OOCR' + LiAlH_4 \longrightarrow R_3Si^*OH \quad (3)$$

TABLE I
R₃Si*OOCR' ENANTIOMERS HAVING THE (+)R₃Si*H CONFIGURATION

Compound	[α]D, solvent	M.p., °C.
(+)R₃Si*OOCCH₃	+18°, pentane	Liq.
(+)R₃Si*OOCC₆H₅	+18°, pentane	Liq.
(+)R₃Si*OOCC₆H₄-*p*(NO₂)	+22°, ether	130
(+)R₃Si*OOCC₆H₃-3,5(NO₂)₂	+23°, ether	Liq.

The product silanol in 3 is necessarily obtained with retention of configuration (plus some racemization of R₃Si*OH during work-up).
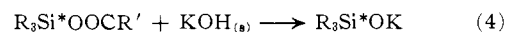
Table II summarizes the results obtained from reduction of the acyloxysilanes with lithium aluminum hydride in ether solvent. The data in Table II comprise a significant change from the predominant *retention* stereochemistry observed for lithium aluminum hydride reduction of optically active silanol, R₃Si*OH; alkoxysilanes, R₃Si*OR' (in which R' is methyl, cyclohexyl, (−)-menthyl, and *t*-butyl); and the disiloxane, R₃Si*OSi*R₃, as reported in a previous paper.[1] It is noteworthy that the present reductions of R₃Si*OOCR' can be carried out at very low temperatures in contrast to, say, R₃Si*O-cyclo-C₆H₁₁, which requires heating at elevated temperatures, above 100°, for several hours. Thus, the change from a poor leaving group to a good leaving group has changed the stereochemistry of lithium aluminum hydride reduction from predominant *retention* to *inversion* of configuration.

TABLE II
LITHIUM ALUMINUM HYDRIDE REDUCTIONS OF R₃Si*OOCR'

Reactant	Temp., °C.	Isolated product(s)	Yield, %	Stereo-specificity[a]
(+)R₃Si*OOCCH₃	−30	(−)R₃Si*H	14	90% inversion
(+)R₃Si*OOCC₆H₅	25	(−)R₃Si*H	48	77% inversion
		(+)R₃Si*OH	26	79% retention
(+)R₃Si*OOCC₆H₅	−78	(−)R₃Si*H	65	90% inversion
(+)R₃Si*OOCC₆H₄-*p*(NO₂)	−78	(−)R₃Si*H	76	84% inversion
(+)R₃Si*OOCC₆H₃-3,5(NO₂)₂	−78	(−)R₃Si*H	62	80% inversion
		(+)R₃Si*OH	30	68% retention

[a] A stereospecificity of, say, 90% means that the product was 80% optically pure (20% racemic), if optically pure reactant was used. If the latter was not optically pure, then the stereospecificity value is adjusted accordingly.

Reactions with KOH(s).—The stereochemistry of the reactions of R₃Si*OR' with potassium hydroxide, KOH(s), containing *ca.* 12% water, has been previously reported.[1] In the present work, this reaction of acyloxysilanes was investigated.

$$R_3Si^*OOCR' + KOH_{(s)} \longrightarrow R_3Si^*OK \quad (4)$$

Again, acyl-oxygen cleavage would yield R₃Si*OK of retained configuration, since the asymmetric center would not be affected, whereas silicon-oxygen cleavage

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(1) For the preceding paper in this series, see: L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Am. Chem. Soc.*, **86**, 3276 (1964).

(2) L. H. Sommer, C. L. Frye, M. C. Musolf, G. A. Parker, P. G. Rodewald, K. W. Michael, Y. Okaya, and R. Pepinsky, *ibid.*, **83**, 2210 (1961).

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

could proceed with inversion or retention of configuration. In that event it was found that the reactions proceed with predominant *inversion* of configuration. The organosilicon products were isolated after conversion of R_3Si^*OK to R_3Si^*OH by hydrolysis—it is known that $(-)R_3Si^*OH$ has the $(-)R_3Si^*H$ configuration,[3] and conversion to the silanol does not affect the asymmetric center. Table III summarizes the results which were obtained with a benzene solvent at 25° for the acetoxysilane, and a xylene solvent at 90° for the other three acyloxysilanes.

TABLE III
REACTIONS OF $(+)R_3Si^*OOCR'$ WITH KOH

Reactant	Product	Yield, %	Stereo-specificity
$(+)R_3Si^*OOCCH_3$	$(-)R_3Si^*OH$	60	85% inversion
$(+)R_3Si^*OOCC_6H_5$	$(-)R_3Si^*OH$	96	75% inversion
$(+)R_3Si^*OOCC_6H_4-p(NO_2)$	$(-)R_3Si^*OH$	79	78% inversion
$(+)R_3Si^*OOCC_6H_3-3,5(NO_2)_2$	$(-)R_3Si^*OH$	100	75% inversion

As in the case of lithium aluminum hydride reductions, the change from alkoxy leaving groups to carboxylate leaving groups engenders a change in the stereochemistry of reaction with $KOH_{(s)}$ from *retention* to *inversion* of configuration. The inversion stereospecificity data in Table III comprise minimum values because of the possibility of some acyl-oxygen cleavage which would give product of retained configuration. The 75-85% inversion of configuration values indicate a maximum of 25% acyl-oxygen cleavage. Thus, with $KOH_{(s)}$, silicon is a more effective electrophilic center than carbonyl carbon.

Reactions with Methanol.—In a pentane solvent, in the presence of cyclohexylamine as an acceptor for formed carboxylic acid, the acyloxysilanes readily undergo methanolysis. Data for the methanolysis reactions are summarized in Table IV.
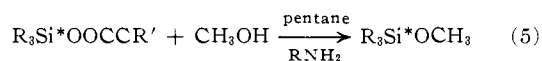
$$R_3Si^*OOCCR' + CH_3OH \xrightarrow[RNH_2]{pentane} R_3Si^*OCH_3 \quad (5)$$

TABLE IV
METHANOLYSES OF $(+)R_3Si^*OOCR'$

Reactant	Product	Yield, %	Stereo-specificity
$(+)R_3Si^*OOCCH_3$	$(-)R_3Si^*OCH_3$	27	87% inversion
$(+)R_3Si^*OOCC_6H_5$	$(-)R_3Si^*OCH_3$	85	84% inversion
$(+)R_3Si^*OOCC_6H_4-p(NO_2)$	$(-)R_3Si^*OCH_3$	82	90% inversion
$(+)R_3Si^*OOCC_6H_3-3,5(NO_2)_2$	$(-)R_3Si^*OCH_3$	88	74% inversion

In reaction 5, with the possible exception of the acetoxysilane, nucleophilic attack at the silicon atom is faster than attack at carbonyl carbon. All four reactions proceed with predominant *inversion* of configuration. In this respect, reaction 5 parallels the methanolysis of R_3Si^*Cl under the same conditions.[3] Indeed, reactions of R_3Si^*Cl with H_2O and with lithium aluminum hydride also proceed with inversion of configuration[3] and there exists, therefore, substantial similarity between -Cl and -OOCR. Both are good leaving groups,[2] and both exhibit a predominant *inversion* stereochemistry in reactions with strong nucleophiles.

The Tosylate Leaving Group.—Many attempts to prepare R_3Si^*OTs from R_3Si^*OK and tosyl chloride were made. All resulted in failure because of the fact that reaction 7 below is much faster than 6.

$$R_3Si^*OK + TsCl \longrightarrow R_3Si^*OTs \quad (6)$$

$$R_3Si^*OTs + R_3Si^*OK \longrightarrow R_3Si^*OSi^*R_3 \quad (7)$$
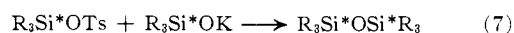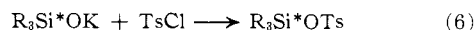
Nevertheless, the stereochemistry of displacement of tosylate from asymmetric silicon with R_3Si^*OK can be determined by examination of the product disiloxane, $R_3Si^*OSi^*R_3$. Reaction 6 does not affect the asymmetric center. For reaction 7, the anticipated results of inversion or retention of configuration are given below for use of $(-)R_3Si^*OK$.

$$(-)R_3Si^*OK + R_3Si^*OTs \xrightarrow[\text{inversion}]{(a)} R_3Si^*OSi^*R_3 \ (meso)$$
$$\xrightarrow[\text{retention}]{(b)} R_3Si^*OSi^*R_3 \quad [\alpha]_D +10°$$
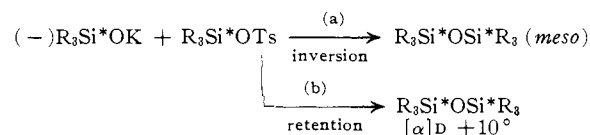
The third possibility, c, that R_3Si^*OTs racemizes at a rate which exceeds its reaction rate with $(-)R_3Si^*OK$, would lead to a 50-50 mixture of the *meso*- and $(+)$-$R_3Si^*OSi'R_3$ having $[\alpha]_D +5°$. $(-)R_3Si^*OK$ and $(+)R_3Si^*OSi^*R_3$ have the same configuration at all three silicon atoms.[1]

It was found that $meso$-$R_3Si^*OSiR_3$ is the product formed in major amount, but that there is also present sufficient active disiloxane to give a rotation for the product of $[\alpha]_D +1.4°$. This corresponds to 86% inversion of configuration and 14% retention of configuration in reaction 7, or to 28% racemization of R_3Si^*-OTs and 100% inversion in reaction 7. Mixture melting point determinations confirmed the formation of essentially *meso*-disiloxane. Thus the stereochemistry of displacement of tosylate from asymmetric silicon proceeds with predominant *inversion* of configuration. In this respect, the tosylate and -Cl leaving groups are similar in their reactions with R_3Si^*OK in xylene.[1]

Mechanism Implications.—In a comprehensive discussion[4] of the mechanism of nucleophilic displacement of good leaving groups from R_3Si^*X with inversion of configuration, the mechanism symbol S_N2-Si was proposed in recognition of certain important differences between S_N2 for carbon and S_N2-Si for silicon. Also, the conclusion was reached that the geometry of S_N2-Si transition states is most probably trigonal bipyramidal with the entering and leaving groups at apical positions and the "bonds" to X and Y long and weak relative to the R–Si bonds.[4] In the present work, the displacements of carboxylate and tosylate groups are examples of reactions proceeding by mechanism S_N2-Si.

It should be noted that carboxylate groups are displaced from asymmetric silicon with inversion of configuration, despite the possibility of a retention stereochemistry resulting from operation of a four-center S_Ni-Si mechanism.[1] Such a possible mechanism would involve
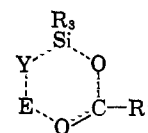
Nevertheless, predominant inversion of configuration is observed, despite the fact that previous work[1] showed that reaction *via* a quasi-six-membered-ring transition state gives retention of configuration. Thus the mechanism of displacement of carboxylate leaving groups from R_3Si^*X is S_N2-Si.

(4) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., in press.

Experimental

Preparation of (+)-α-Naphthylphenylmethylacetoxysilane, (+)-R₃Si*OOCCH₃.—Potassium silanolate,[1] (−)R₃Si*OK, in xylene solvent reacted rapidly with acetyl chloride to give a 100% yield of (+)R₃SiOOCCH₃. The product, [α]D +17.7°, was isolated by removal of xylene and excess acetyl chloride under vacuum, leaving a residue which was taken up in hexane. After decanting from the potassium chloride and removal of hexane, there was obtained 2.3 g. of liquid product. The infrared spectrum was identical with that of racemic acetoxysilane prepared from inactive R₃SiCl and potassium acetate,[5] and had the following bands attributed to the Si–OOCCH₃ moiety: 5.79, 7.30, 8.05, 9.83, and 10.73 μ.[6]

Anal. Calcd. for C₁₉H₁₈O₂Si: Si, 9.2; sapon. equiv., 306.4. Found: Si, 9.1; sapon. equiv., 305.7.

Preparation of (+)-α-Naphthylphenylmethylbenzoxysilane, (+)R₃Si*OOCC₆H₅.—Reaction of (−)R₃Si*OK and benzoyl chloride in xylene solvent gave an immediate precipitate of colloidal potassium chloride. The product, 1.81 g., was isolated as a colorless, viscous liquid having [α]D +17.7° (c 8.6 in pentane), in 64% yield. The structure was confirmed by an infrared spectrum and analyses for silicon. Infrared maxima characteristic of the Si–OOCC₆H₅ moiety are: 5.90, 6.35, 6.90, 7.65, 7.85, 8.55, 9.15, 9.40, and 11.80 μ.

Anal. Calcd. for C₂₄H₂₀O₂Si: Si, 7.60. Found: Si, 7.63.

Preparation of (+)-α-Naphthylphenylmethyl-p-nitrobenzoxysilane, (+)R₃Si*OOCC₆H₄-p(NO₂).—From (−)R₃Si*OK and p-nitrobenzoyl chloride the product was obtained in 87% yield as 1.04 g. of crystalline material having m.p. 130°, [α]D +22° (c 564 in ether). The structure was confirmed by infrared spectrum and analyses. Infrared bands characteristic of a p-nitrobenzoxy group attached to silicon are: 5.85, 6.25, 6.55, 7.45, 7.80, 9.10, 9.85, 11.45, and 11.60 μ.

Anal. Calcd. for C₂₄H₁₉NO₄Si: Si, 6.79. Found: Si, 6.86.

Preparation of (+)-α-Naphthylphenylmethyl-3,5-dinitrobenzoxysilane, (+)R₃Si*OOCC₆H₃-3,5(NO₂)₂.—From (−)R₃Si*OK and 3,5-dinitrobenzoyl chloride the product was obtained as 1.09 g. (82% yield) of yellow viscous oil having [α]D +23° (c 5.1 in ether). The structure was confirmed by infrared spectrum and analyses; infrared maxima characteristic of a 3,5-dinitrobenzoxy group attached to silicon: 5.85, 6.20, 6.50, 6.90, 7.50, 7.85, 8.60, 9.35, and 10.90 μ.

Anal. Calcd. for C₂₄H₁₈N₂O₆Si: Si, 6.12. Found: Si, 6.33.

Lithium Aluminum Hydride Reductions of R₃Si*OOCR′.—Reduction of the (+)-benzoxysilane will be described in detail as being typical of the procedure used. To 2.0 g. of lithium aluminum hydride and 25 ml. of dry ether was added 1.5 g. (4.1 mmoles) of (+)-benzoxysilane, [α]D +12.6°, dissolved in 35 ml. of ether. The reaction was slightly exothermic. After addition, the reaction mixture was stirred for 45 min. Excess hydride was decomposed with acetone and the contents of the flask were then poured into a separatory funnel containing cold, dilute ammonium chloride solution. The organic phase was extracted twice with ammonium chloride solution, three times with water, and then dried over anhydrous sodium sulfate. Removal of the solvent under vacuum afforded 0.92 g. of an oil having [α]D −5.1° (c 5.2 in pentane). The infrared spectrum (neat) showed the presence of approximately equal amounts of R₃Si*H (4.7 μ for Si–H) and R₃Si*OH (2.8, 3.0 μ for O–H). The silane and silanol were separated by chromatography over a 30 × 1 in. column of silica gel. Elution with 250 ml. of 50% benzene–pentane yielded, upon solvent removal, 0.48 g. (48% yield) of (−)R₃Si*H, [α]D −13° (c 2.8 in pentane). Further elution with 200 ml. of ether yielded 0.28 g. (26% yield) of (+)R₃Si*OH, [α]D +8.8° (c 1.7 in ether). Since the (+)-benzoxysilane had a maximum optical purity of 71% (12.6 × 100/17.7), and the product R₃Si*H and R₃Si*OH had optical purities of 37 and 44%, the stereospecificity values given in Table II obtain.

Reduction of (+)-benzoxysilane, [α]D +15.8°, at −78° increased the yield of R₃Si*H to 65%. There was obtained (−)-R₃Si*H (0.96 g.) having [α]D −24.5° (c 3.2 in pentane) and only ca. 0.1 g. of racemic silanol. Active silanol is partially racemized

(5) The preparation of acyloxysilanes from metal carboxylates and chlorosilanes is known; cf. A. J. Barry, U. S. Patent 2,405,988 (1946).

(6) For the preparation of triphenylacetoxysilane from sodium triphenylsilanolate and acetyl chloride, see N. S. Nametkin, A. V. Topchiev, and F. F. Machus, *Dokl. Akad. Nauk SSSR*, **87**, 233, 705 (1952); *Chem. Abstr.*, **47**, 12281, 2723 (1953).

by chromatography over silica gel and is also sensitive to dilute aqueous acid.

Reduction of (+)-acetoxysilane, [α]D +12.6°, at −30° gave a 14% yield (0.63 g.) of R₃Si*H having [α]D −24.2° (c 2.86 in pentane). The silanol was not isolated.

Reduction of (+)-p-nitrobenzoxysilane, [α]D +22.2° (c 3.7 in ether), at −78° gave a 76% yield (9.32 g.) of R₃Si*H, [α]D −23° (c 1.6 in pentane).

Reduction of (+)-3,5-dinitrobenzoxysilane, [α]D +22.9° (c 5.5 in ether), at −78° gave a 62% yield (9.34 g.) of (−)R₃Si*H, [α]D −20.4° (c 2.3 in pentane), and (by ether elution) a 30% yield (9.18 g.) of (+)R₃Si*OH, [α]D +7.4° (c 2.2 in ether).

Reactions with KOH(s).—Reaction of KOH(s) with the (+)-benzoxysilane will be described in detail as being typical of the procedure used. (+)-α-Naphthylphenylmethylbenzoxysilane (0.81 g., 2.2 mmoles), [α]D +17.7° (c 8.6 in pentane), was dissolved in 35 ml. of xylene and 4.0 g. of powdered potassium hydroxide was added. The reactants were then heated on the steam bath for 10 min. The mixture was cooled, transferred to a separatory funnel, and after addition of ether (75 ml.) was washed three times with cold water. After drying over anhydrous sodium sulfate, the solvent was removed from the ether solution to give 0.56 g. (96% yield) of (−)R₃Si*OH), [α]D −10° (c 2.5 in pentane). Optically pure silanol[1] has [α]D 20°. The infrared spectrum showed typical O–H absorption (2.8, 3.0 μ) and the usual bands for the α-naphthylphenylmethylsilyl group.[3] Since optically active silanol is quite sensitive toward racemization by aqueous acid or base, the stereospecificity values given in Table III are probably significantly lower than the real values.

Reaction of (+)-acetoxysilane, [α]D +15.0° (c 5.46 in pentan), gave a 60% yield (0.79 g.) of (−)R₃Si*OH, [α]D −12° (c 8.2 in ether).

Reaction of (+)-p-nitrobenzoxysilane, [α]D +22.8° (c 6.3 in xylene), gave a 79% yield (0.52 g.) of (−)R₃Si*OH, [α]D −12° (c 3.0 in ether).

Reaction of (+)-3,5-dinitrobenzoxysilane, [α]D +20° (c 6.2 in xylene), gave a 100% yield (0.61 g.) of (−)R₃Si*OH, [α]D −11° (c 2.4 in ether).

Methanolysis Reactions.—Reaction of methanol with (+)-benzoxysilane in pentane solvent will be described in detail as being typical of the procedure used. Purified pentane, 100 ml., 1.5 ml. of cyclohexylamine, and 1.0 ml. of dry methanol (25 mmoles) were placed in a flask. Then a solution of (+)-benzoxysilane (1.70 g., 4.6 mmoles), [α]D +14.6° (c 6.7 in pentane), dissolved in 15 ml. of pentane was added. The solid was filtered after 5 min. and the filtrate was collected in a separatory funnel. Following one extraction with cold water and drying over anhydrous sodium sulfate, the pentane solution was concentrated on the steam bath. Unreacted cyclohexylamine was removed at 1 mm. pressure with heating to give (−)R₃Si*OCH₃, 1.09 g., 85% yield, [α]D −9.95° (c 5.5 in pentane). The (−)-methoxysilane had an infrared spectrum identical with that of authentic methoxysilane.[3] Optically pure methoxysilane has [α]D 17° (pentane), and the starting benzoxysilane was 82% optically pure.

Methanolysis of (+)-acetoxysilane, [α]D +16° (c 1.7 in pentane), gave a 27% yield (0.25 g.) of (−)R₃Si*CH₃, [α]D −12.2° (c 2.06 in pentane).

Methanolysis of (+)-p-nitrobenzoxysilane, [α]D +22° (c 3.6 in ether), was carried out as described above, except that benzene, instead of pentane, was used as the solvent. There was obtained an 82% yield of (−)R₃Si*OCH₃, 0.40 g., having [α]D −14° (c 2.7 in pentane).

Methanolysis of (+)-3,5-dinitrobenzoxysilane, [α]D +22.8° (c 4.2 in ether), was carried out in 25% benzene–pentane solvent. There was obtained an 88% yield (0.56 g.) of (−)R₃Si*OCH₃, [α]D −8.6° (c 3.5 in pentane).

Reaction of (−)R₃Si*OK with Tosyl Chloride.—To a 250-ml. flask was added 20 ml. of a 0.31 N xylene solution of (−)R₃Si*OK (6.16 mmoles) having [α]D −69.8° (c 9.3 in xylene). To this solution, a xylene solution (10 ml.) of p-tosyl chloride (0.587 g., 3.08 mmoles) was added. When approximately one-half of the tosyl chloride solution had been added, a white precipitate began to form. Also, the reaction was slightly exothermic. After the mixture had been swirled for a moment, 150 ml. of pentane was added to precipitate the solid. The solid was filtered and the filtrate and washings were collected in a separatory funnel. The organic phase was washed four times with cold water and dried over anhydrous sodium sulfate. Solvent removal gave a crude product, 1.03 g., having [α]D +1.4 ± 0.2° (c 6.0 in pentane). Purification by chromatography over silica gel yielded 1.20 g. of a

very viscous sirup which hardened to a glass on cooling. This material had $[\alpha]D$ +1.27° (c 5.3 in pentane). It was identified as disiloxane by its infrared spectrum as compared to authentic disiloxane.[1] The yield was 66%. Crystallization and recrystallization from pentane gave white crystals (0.31 g.), m.p. 96–98°. A mixture m.p. with authentic *meso*-R₃Si*OSi*R₃ showed no depression (authentic *meso*-disiloxane prepared from reaction of

(−)R₃Si*OK with (−)R₃Si*Cl). A 50–50 mixture of the reaction product and racemic (+)R₃Si*OSi*R₃ (racemic siloxane prepared by mixing equal amounts of (+)- and (−)-enantiomers) had m.p. 85–95°.

Cyclopropanes. XV. The Optical Stability of 1-Methyl-2,2-diphenylcyclopropyllithium[1]

By H. M. Walborsky, F. J. Impastato, and A. E. Young

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Halogen–lithium interchange between (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane and *n*-butyllithium produced 1-methyl-2,2-diphenylcyclopropyllithium which on treatment with carbon dioxide, bromine, and iodine yielded products in which the configuration as well as the optical activity had been completely retained. No effect on the optical results could be found on varying the temperature, solvent, or reaction time. The lithium derivative was found to react with solvent in the order 1,2-dimethoxyethane > tetrahydrofuran > diethyl ether.

Introduction

Previous studies on the optical stability of tetrahedrally (sp³) hybridized organolithium compounds have revealed that their stability is both temperature and solvent dependent. Letsinger[2] showed that halogen–metal interchange between (−)-(R)-2-octyl iodide and *sec*-butyllithium at −70° followed by carbonation gave (−)-(R)-2-methyloctanoic acid which was 80% racemized. It was also demonstrated that a small amount of diethyl ether (∼6%) in the petroleum ether solvent was required for the halogen–metal interchange to occur and furthermore the optical purity decreased with increased temperature and time alloted for the exchange. The latter observations were also made by Curtin and Koehl[3] in their study on the exchange between (±)-2-octyllithium and di-(−)-(R)-*sec*-butylmercury which yields on carbonation (−)-(R)-2-methylbutyric acid. This exchange occurs in pentane solution and diethyl ether is not necessary to effect it. As a matter of fact when 6% of diethyl ether is added the product obtained is racemic whereas when pentane alone is the solvent the product is 20–30% optically pure. The effect of diethyl ether may well be to cause dissociation of the carbon–lithium bond which then results in racemization. This would be consistent with observations made on the amines which are isoelectronic with the tetrahedrally hybridized carbanions. In the case of amines there is no gegenion available and consequently there is a very rapid inversion of configuration.

Trigonally hybridized vinyllithium derivatives have been shown to retain their configuration to a much larger extent than tetrahedrally hybridized ones, although substituent, solvent, and temperature effects have also been observed.[3,4] Miller and Lee[5] have

established lower limits to the activation energy for the isomerization of vinyl carbanions formed from 1,2-dihaloethenes as 25–35 kcal./mole.

With trigonally hybridized nitrogen, stereoisomeric forms of oximes[6] and azomethines[7] have been isolated which demonstrate that the trigonally hybridized nonbonded pair of electrons is capable of maintaining its configuration. This is illustrated by the observation that the oxime of 4-ketocyclohexanecarboxylic acid could be resolved into its optically active enantiomers.[8] Curtin and Hausser[9] have recently studied the kinetics of *cis–trans* isomerization of a number of stereoisomeric imines and have found that, as in the case of vinyl anions, substituents capable of delocalizing a negative charge have a marked influence on the rate of isomerization.

The cyclopropane ring has been characterized as having a great deal of "double bond character."[10] The stereochemical fate of a pair of nonbonding electrons in an orbital which is part of a three-membered ring poses an interesting question. Would the cyclopropyl carbanion whose exocyclic orbitals are reported[11] to be sp²·²⁸ hybridized behave like the trigonally hybridized (sp²) vinyl carbanion or the tetrahedrally hybridized (sp³) carbanion? In an attempt to answer this question, optically active 2,2-diphenylcyclopropyl cyanide (I) was treated with lithium diisopropylamide in ether. Under these conditions racemization was rapid.[12] However, a comparison of the rate of racemization of I. by methoxide in methanol, with the acyclic analog 1-methyl-2,2-diphenylpropionitrile indicated that a barrier to inversion did exist since the latter racemized 1.2 × 10³ faster than I.[13] The existence of this energy barrier to inversion was reinforced

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