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OPTICALLY ACTIVE SILANES AND THEIR REACTIONS: THE PERHYDROMETHYL-1-NAPHTHYLPHENYLSILYL SYSTEM*

GLEN R. BUELL, LEONARD SPIALTER AND J. DUDLEY AUSTIN**
Chemistry Research Laboratory, Aerospace Research Laboratories, Office of Aerospace Research, Wright-Patterson AFB, Ohio 45433 (U.S.A.)

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SUMMARY

The first reported aliphatic silyl system optically active at silicon has been prepared by the catalytic hydrogenation of the methyl-1-naphthylphenylsilyl system, (R_3Si^*–). Both the menthoxy and the fluoro derivative of R_3Si^*– have been found to proceed smoothly to the perhydro derivative ($R_3^HSi^*$–). Isomers were observed due to the four possible *cis/trans* configurations of the perhydro-1-naphthyl group. Reactions of the $R_3^HSi^*$– assemblage were found, in general, to be stereospecific and to conform to the rules of stereospecific reactions at silicon as proposed by Sommer. A significant exception to the high degree of stereoselectivity generally exhibited by the $R_3^HSi^*$-system was the hydrolysis of $R_3^HSi^*Cl$ to form the silanol. In a series of runs the resulting silanol was found to vary from 0 to 21% in optical purity.

INTRODUCTION

Most silicon stereochemical work has been performed on the methyl-1-naphthylphenylsilyl system (herein symbolized as R_3Si–) which was first resolved as the menthoxide (I) by Sommer and Frye[1]. Reactions of this system have been shown to proceed with a high degree of stereospecificity, with examples of both inversion and retention of configuration being observed[1-9].

For poor (highly basic) leaving groups Sommer has correlated the data in terms of retention and inversion mechanism models whose operation is sensitive to the nature of the reagent and the solvent. For good leaving groups, the S_N2-Si stereochemistry rule of inversion of configuration for acyclic systems has been found to apply[10]. Both the configurationally retentive and invertive mechanisms are pictured as proceeding through pentacoordinate transition states. For the invertive mechanism, the entering and the leaving groups, X and Y in Fig. 1, would occupy the axial positions of a trigonal bipyramid. With either the entering or leaving group in the axial position and the other in the equatorial position of a trigonal bipyramid or with the two groups

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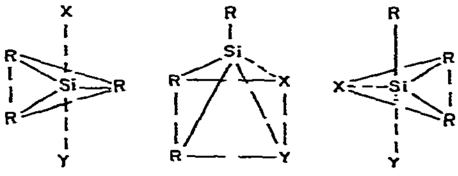
** Visiting Research Associate under contractual arrangement with The Ohio State University Research Foundation, presently employed at The Dow Corning Corp., Midland, Michigan.

in adjacent corner positions of a square pyramid structure, retention of configuration would be expected (Fig. 1)*.

Other systems made available through the stereospecific aromatic bromodesilylation as described by Eaborn[11] and by the resolution of menthoxy-1-naphthylphenylvinylsilane into its diastereomers by Davydova[12], have been somewhat less extensively studied by Sommer[13] and Corriu[14], respectively.



INVERSION RETENTION RETENTION

Fig. 1. Pentacoordinate transition states.

The role of steric effects on the course of reaction at silicon has been little considered. However, it seems logical that steric requirements can influence the position of the entering and leaving groups in the pentacoordinate transition state and therefore the steric course of the reaction. Indeed, exceptions to Sommer's rules arising entirely from the structural requirements of the molecule are observed in the facile hydrolysis of 1-chloro-1-silabicyclo[2.2.1]heptane[15] and 1-chloro-1-silabicyclo[2.2.2]octane[16]. Due to uniquely constrained structures these compounds must react by a retentive mechanism, even though the Cl group is classed as a good leaving group and therefore should undergo invertive displacement**.

The resolution of optically active silyl systems has proven difficult. However, hydrogenation of existing asymmetric arylsilanes would be a convenient method for preparing new optically active silicon compounds with increased steric crowding of the groups attached to silicon. The catalytic hydrogenation of an appropriate member of the resolved methyl-1-naphthylphenylsilyl system would not only produce a new optically active silyl system for the study of bulk effects on the course of reaction at silicon, but in addition would provide a resolved system, optically active at silicon, which contains no aromatic or unsaturated groups. Once its stereochemical reactive paths are known, such an aliphatic silyl system would also be useful for the investigation of reactions where aromaticity or unsaturation can lead to undesirable side reactions. Hydrogenation of the 1-naphthyl group does have certain disadvantages in that the resulting product can exist in four geometric configurations (Fig. 2), which

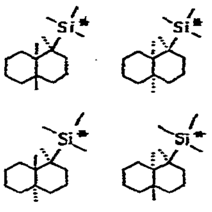


Fig. 2. Isomers of 1-substituted decalin.

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* An excellent discussion of the stereochemistry of reactions at silicon is provided by Sommer in ref. 17.

** A general discussion of reactions at bridgehead silicon can be found in chapter 9 of ref. 17.

could possibly affect the course of reactions at the Si atom. The investigation of possible isomeric effects and the general reaction of this aliphatic silyl system are described below.

RESULTS AND DISCUSSION

The catalytic hydrogenation of I (R_3Si^*O–menth) to form its perhydro derivative (II) ($R_3^HSi^*O$–menth) was easily accomplished (Fig. 3), and thin layer chromatograph of the product produced three distinct bands. Each of the materials extracted from these bands was optically active and each analysed correctly for II. In order to insure that the stereochemistry of the fractions of II were identical, a small amount of each was isolated by means of preparative layer chromatography. When the compounds were successively reduced to the silane (III) with $LiAlH_4$, treated with Cl_2 to form the chloride (IV) and again reduced to III with $LiAlH_4$ (Fig. 4) it was found that they all retained their optical activity and the sign of rotation after treatment with each reagent was the same for each of the isomers.

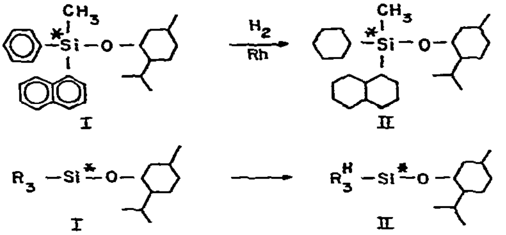

Fig. 3. Hydrogenation of menthoxymethyl-1-naphthylphenylsilane.

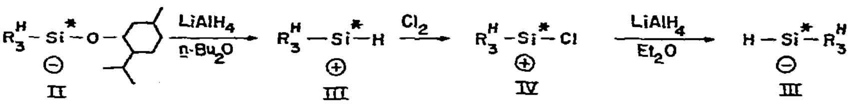

Fig. 4. Reactions of $R_3^HSi^*$– compounds.

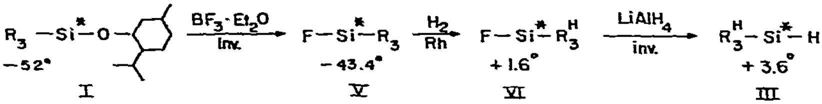

Fig. 5. Stereospecific synthesis path for perhydromethyl-1-naphthylphenylsilane.

Since all of the isomers of the $R_3^HSi^*$– group exhibit the same stereochemistry the laborious separation procedure can be eliminated and all subsequent studies were performed on the mixture of isomers. The reduction of II with $LiAlH_4$ was found to be an extremely slow reaction (refluxing for one week in butyl ether did not carry the reaction to completion). A more convenient route was found by first converting I to the fluoride (V) before hydrogenation. The hydrogenated fluoride (VI) was found to react readily with $LiAlH_4$ to give the mixture of silanes (III) (Fig. 5). III was then converted to IV, which was then transformed to the III and the silanol (VII) by reduction and hydrolysis, respectively (Fig. 6).

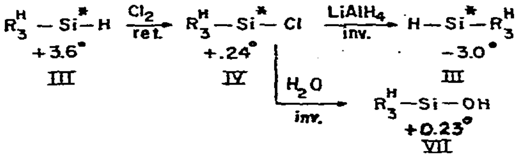

Fig. 6. Stereochemistry of the perhydromethyl-1-naphthylphenylsilyl system.

Throughout this work, the configurations of the $R_3^HSi^*-$ compounds were checked by means of optical rotatory dispersion and the course (retention or inversion) of each reaction was determined. While it is not argued that this method in itself can be regarded as giving absolute proof of configuration, it was found to be consistent within itself for this series of compounds and with the few cases where the configuration was known with a high degree of certainty. The stereochemistry of R_3Si^*- and $R_3^HSi^*-$ are compared in Table 1 and the $R_3^HSi^*-$ compounds having (+)-R_3Si^*H configuration are listed in Table 2.

With the exception of the hydrolysis of the chloride, the stereochemistry of $R_3^HSi^*-$ parallels that of the R_3Si^*- system as determined by Sommer and proceeds with a high degree of stereospecificity. This one exception is particularly noteworthy in that it results in a compound of low optical purity or in a racemic mixture under conditions in which similar silanes have been reported to maintain a high degree of optical integrity. In a series of four runs the silanol resulting from hydrolysis of IV ranged from zero to 21%* in optical purity and the reaction was found to proceed by

TABLE 1

STEREOCHEMISTRY OF THE R_3Si^*- AND $R_3^HSi^*-$ SYSTEMS

Reactant	Reagent	R_3Si^*-	$R_3^HSi^*-$
-O-menth	$LiAlH_4$	Retention	Retention
-H	Cl_2	Retention	Retention
-Cl	$LiAlH_4$	Inversion	Inversion
-F	$LiAlH_4$	Inversion	Inversion
-Cl	H_2O	Inversion	Inversion

TABLE 2

COMPOUNDS HAVING THE (+)-R_3SiH CONFIGURATION

Compound	$[\alpha]_D^{20}$ in CCl_4 (°)
(+)-R_3^HSiF	+1.6
(+)-R_3^HSiH	+3.6
(+)-R_3^HSiCl	+0.24
(−)-R_3^HSiOH	−1.1[a]

[a] Unpublished value for $R_3^HSi^*OH$ made by ozonolysis of $R_3^HSi^*H$.

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* $R_3^HSi^*OH$ has been prepared by the reaction of $R_3^HSi^*H$ with ozone. This ozonolysis reaction will be reported at a later date with related material. The silanol prepared by ozonolysis was assumed to be 100% optically pure for comparison purposes.

an invertive mechanism. When the identical technique was employed with R_3Si^*Cl the $[\alpha]_D^{20}$ of the resulting R_3Si^*OH was consistently found to be >95% of the value reported by Sommer[2]. $R_3^HSi^*OH$ has been shown to retain 96% of its optical activity when treated under conditions identical to those used for hydrolysis of the chloride, thereby virtually eliminating the possibility of a highly stereospecific hydrolysis reaction followed by the racemization of the active silanol. The implications of the low degree of stereospecificity in the hydrolysis of $R_3^HSi^*Cl$ are not clear at this time. It is noteworthy that Corriu and Masse[18] have recently reported a lack of stereoselectivity in the hydrolysis of 1,2,3,4-tetrahydro-2-chloro-2-(1-naphthyl)-2-silanaphthalene. However, models indicate that due to the constrained ring structure of this newly reported system, invertive displacement would be more difficult than in the $R_3^HSi^*$– system and therefore a direct comparison should probably be avoided. New asymmetric silyl systems are being designed to further elucidate the steric and electronic factors in stereoselective reactions at silicon. The interesting R_3^HSiOH system is being further investigated with respect to synthesis and stereochemistry and the results will be described at a later date.

EXPERIMENTAL

General

Materials. All commercial chemicals were used without further purification unless otherwise noted.

Equipment and apparatus. Optical rotations were measured on a O. C. Rudolph and Sons model #304 polarimeter. Optical rotatory dispersion curves were taken on a Bendix Polarmatic Recording Spectropolarimeter. All rotations were taken at 20°. Optical rotatory dispersion curves were first run on the solvent and then the solution, and the deviation from the solvent curve was noted. Compounds with the same direction of deviation were considered to have the same configuration.

Analyses. All microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Menthoxymethyl-1-naphthylphenylsilane (I)

I was prepared and separated into its diastereomers by the method of Sommer[2]. Material prepared in this manner had an $[\alpha]_D^{20}$ $-52°$ (*c* 2.4 in CCl_4), lit. $[\alpha]_D$ $-53.9°$ (*c* 11.32 in cyclohexane).

Perhydromenthoxymethyl-1-naphthylphenylsilane (II)

Five g of I, 2 g of 5% Rh on charcoal, and 150 ml of methylcyclohexane were placed into a 300-ml stainless steel stirred reactor. The mixture was stirred for 30 h at 170 atm of H_2 pressure and 125°. After the catalyst had been removed by filtration, the solvent was stripped at reduced pressure. The resulting clear viscous liquid was separated into its components by means of preparative layer chromatography on Merck silica gel $PF_{254-366}$ using 10% benzene in hexane as the eluting solvent. Three distinct bands were obtained and their respective compounds were extracted from the silica gel with benzene. Each of these compounds was found to be optically active and the IR, UV and NMR spectra indicated that no aromatic groups were present. (Found: C, 77.74; H, 12.09; Si, 6.80. Found: C, 77.65; H, 11.92; Si, 6.79. Found:

C, 77.61; H, 12.00; Si, 6.62. $C_{27}H_{40}OSi$ calcd.: C, 77.51; H, 11.96; Si, 6.70%.) The three isolated compounds are believed to be isomers resulting from the four possible *cis* and *trans* configurations of 1-substituted decalin compounds. No attempt was made to determine the configuration of these isomers.

Perhydromethyl-1-naphthylphenylsilane (III)

(*a*) *By reduction of II with $LiAlH_4$.* In a typical reaction 5 g of the isomeric mixture of II (0.012 mole), 5 g of $LiAlH_4$ (0.13 mole) and 100 ml of n-butyl ether were heated at reflux for 7 days. The excess $LiAlH_4$ was destroyed by the addition of acetone and the inorganic salts were extracted with water. The mixture was then dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. Purification of the mixture by preparative layer chromatography on silica gel, using 5% benzene in hexane as the eluting solvent, yielded 0.5 g (16% of theory) of the colorless liquid silane $[\alpha]_D^{20}$ +4.2° (*c* 30.7 in CCl_4). (Found: C, 77.47; H, 12.39, Si, 10.41. $C_{17}H_{32}Si$ calcd.: C, 77.19; H, 12.12; Si, 10.62%.)

(*b*) *By reduction of perhydrofluoromethyl-1-naphthylphenylsilane* (V) *with $LiAlH_4$.* The procedure used was identical to that reported by Sommer for the reduction of fluoromethyl-1-naphthylphenylsilane[2]. When five grams of V were reduced, the yield of III $[\alpha]_D^{20}$ +3.6° (*c* 31.5 in CCl_4) was 4.6 g (96% of theory).

(*c*) *By reduction of perhydrochloromethyl-1-naphthylphenylsilane* (IV). The experimental conditions were the same as those described by Sommer for the reduction of the analogous aromatic chloride[2]. In this manner, 3 g of IV $[\alpha]_D^{20}$ −0.24° (*c* 41.7 in CCl_4) was quantitatively converted to III $[\alpha]_D^{20}$ −3.0° (*c* 26.9 in CCl_4).

Perhydrochloromethyl-1-naphthylphenylsilane (IV)

Chlorinations were carried out as described by Sommer for the aromatic analog[2]. Two grams of III $[\alpha]_D^{20}$ +3.6° when treated with chlorine were quantitatively converted to IV $[\alpha]_D^{20}$ +0.24° (*c* 41.7 in CCl_4). (Found: C, 68.51; H, 10.69; Si, 9.61. $C_{17}H_{31}ClSi$ calcd.: C, 68.29; H, 10.45; Si, 9.39%.)

Fluoromethyl-1-naphthylphenylsilane (V)

This compound was made according to the procedure of Sommer[2]. The resulting product had a rotation of $[\alpha]_D^{20}$ −43.4° (*c* 42.8 in CCl_4).

Perhydrofluoromethyl-1-naphthylphenylsilane (VI)

A 300-ml stirred pressure reactor was charged with 5.0 g of V (0.019 mole), 2 g of 5% Rh on charcoal and 150 ml of methylcyclohexane. The mixture was stirred at 125° and 170 atm/H_2 for 20 h. The catalyst was removed by filtration and the solvent was stripped under reduced pressure. The yield of the clear viscous liquid VI was 5.1 g (96% of theory) $[\alpha]_D^{20}$ −1.6° (*c* 36.6 in CCl_4). (Found: C, 72.51; H, 11.12; Si, 9.60. $C_{17}H_{31}FSi$ calcd.: C, 72.27; H, 11.06; Si, 9.94%.)

Perhydromethyl-1-naphthylphenylsilanol (VII)

The procedure reported by Sommer for the preparation of methyl-1-naphthylphenylsilanol by the hydrolysis of chloromethyl-1-naphthylphenylsilane[2] was used. Thus when 2 g of IV $[\alpha]_D^{20}$ 0.24° in ether solution was shaken with cold water, washed with water and dried over sodium sulfate, there was obtained upon removal of the solvent, 1.7 g (91% of theory) of the liquid VII. (Found: C, 72.66; H, 11.48; Si, 9.86. $C_{17}H_{32}OSi$ calcd.: C, 72.78; H, 11.49; Si, 10.01%.) The resulting compound was not optically active. In four such runs the highest rotation obtained was $[\alpha]_D^{20}$ +0.23° (*c* 5.16 in CCl_4), corresponding to 21% optically purity. ($[\alpha]_D^{20}$ 1.1° from $R_3^HSi^*OH$ prepared from ozonolysis of $R_3^HSi^*H$ taken as optically pure.)

Optical stability of $R_3^HSi^*OH$ to hydrolysis conditions

A 1.6 g sample of VII, $[\alpha]_D^{20}$ 0.23° in 100 ml of ether was poured into a 500 ml separatory funnel containing 100 ml of 0.05 *N* HCl and was shaken vigorously for 2 min. The mixture was allowed to stand at room temperature for 2 h and then was worked up in the same manner described for the hydrolysis of IV. The recovered silanol had a rotation $[\alpha]_D^{20}$ 0.22° (96% of the original rotation).

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