same when the solutions are prepared and spectra run at room temperature. On cooling anisole–$FSO_3H$ acid solutions whose room temperature spectra were identical with the published spectra ($\delta(CH_3) = 4.4$ ppm) to $-60°$, no change in the spectra could be observed.[5] Inasmuch as the $CH_3$ nmr resonance of *para*-protonated anisole in other solvents occurs near 4.8 ppm,[1,2] and the methyl resonances of methoxyalkyl cations in general occur between 4.8 and 5.2 ppm,[6] the published and observed nmr spectra of anisole in either $FSO_3H$ or $H_2SO_4$ at room temperature are inconsistent with that expected of the *para*-protonated anisole.

The ultraviolet spectrum of anisole in 92% $H_2SO_4$, prepared either by adding anisole to cold 92% $H_2SO_4$ or by diluting anisole in 98% $H_2SO_4$, is in all details independent of its mode of preparation and, except for a slight blue shift ($\approx 1$ mμ), identical with spectra in 98% $H_2SO_4$. On diluting anisole–$H_2SO_4$ solutions to 80% water, the 284-mμ band is transformed, with little change in molar extinction coefficient, into a typical aromatic band ($\lambda_{\max}$ 278 mμ), with the disappearance, or large blue shift, of the 240-mμ band. Virtually identical solvent effects may be observed in the ultraviolet spectrum of toluenesulfonic acid, $\lambda_{\max}$ ($H_2SO_4$) 271, 262, and 237 mμ; $\lambda_{\max}$ ($H_2O$) 259 mμ.

Finally, we are unable to recover anisole detectable by vpc from anisole–$H_2SO_4$ or –$FSO_3H$ acid solutions after drowning on ice when the solutions are more than a minute or so old. Indeed we have found, by the simple expedient of noting the presence or absence of a cloudy solution after pouring anisole–$H_2SO_4$ into water, that sulfonation of anisole in 92% or greater $H_2SO_4$ is complete at room temperature in a matter of seconds. A high-boiling water-insoluble product may be recovered from anisole–$FSO_3H$. This product gives a single peak on vpc at 210° on an SE-30 column. The infrared and nmr spectra indicate this product to be almost entirely *ortho*-substituted anisole; presumably by analogy with the known reaction in $ClSO_3H$, the product is *o*-anisylsulfonyl fluoride.

In conclusion, the published nmr spectrum[1b] of anisole in $FSO_3H$ at room temperature and the ultraviolet maxima at 284 and 240 mμ in $H_2SO_4$ may not be assigned to *para*-protonated anisole. On the basis of known reactions, comparison of solvent effect on ultraviolet spectra, nmr spectra, and the high water solubility of products from $H_2SO_4$, the species responsible for these spectra almost without doubt are anisyl sulfonation products. It has already been reported[7] that *p*-methylanisole and *p*-anisylamine have sulfonation half-lives of less than 1 min in concentrated sulfuric acid at room temperature.

Given the above conclusions, the question remains, does the absence of a new maximum at wavelengths greater than 270 mμ in the spectra of anisole in more dilute $H_2SO_4$ and $HClO_4$ acid preclude *para* C protonation of anisole in these systems? Kesege and Hakka[4] have assigned a *shoulder* which appears at 285 mμ in the spectrum[8] of anisole in concentrated $HClO_4$ to the *para*-protonated species. This assignment[4] is based on a predicted $\lambda_{\max}$ 285 mμ obtained by extrapolation of data from more highly substituted alkoxybenzenes which are C protonated.

On the other hand, Ramsey and Taft[6] have reported that the ultraviolet spectra of $R_2C^+OR'$ ions are largely independent of whether $R'$ is H or $CH_3$. Therefore, we feel O-protonated 1,4-cyclohexadienone in $H_2SO_4$ should be an excellent model for *para*-C-protonated anisole. The ultraviolet $\lambda_{\max}$ for 1,4-cyclohexadienone is not available, but the ultraviolet maximum of 6,6-dimethyl-1,4-cyclohexadienone in methanol has been reported[9] as 227 mμ. Application of the $CH_3OH \rightarrow H_2SO_4$ solvent correction obtained[10] from mesityl oxide (4-methyl-3-pentenone) of $-20$ kcal/mole to $\lambda_{\max}$ 227 mμ and correcting for alkyl substitution predicts an ultraviolet $\lambda_{\max} < 270$ mμ for the ultraviolet spectrum of *para*-protonated anisole. We consider this estimate of the ultraviolet absorbtion maxima of *para*-C-protonated anisole to be only a little less speculative than that of Kesege and Hakka, and suggest that currently available spectral data do not permit an unambiguous assignment of O or C protonation of anisole in aqueous acid systems at room temperature.

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(5) We have been able to reproduce the low-temperature spectra of anisole in $FSO_3H$ by preparing the solutions at $-80°$ and running the spectra at $-60°$. Above 0° the 4.8-ppm $CH_3$ resonance rapidly irreversibly disappears and is replaced with a second band at 4.4 ppm. We have no trouble reproducing the anisole $SbF_5$–$FSO_3H$ spectra of ref 1a.

(6) B. G. Ramsey and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 3058 (1966).

(7) P. Schleyer, D. Kleinfelter, and H. Richey, Jr., *ibid.*, **85**, 479 (1963).

(8) K. Yates and H. Wai, *Can. J. Chem.*, **43**, 2131 (1965).

(9) S. Winstein and R. Baird, *J. Am. Chem. Soc.*, **85**, 567 (1963).

(10) S. Nagakura, A. Minegishi, and K. Stanfield, *ibid.*, **79**, 1033 (1957).

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## Stereochemistry of Asymmetric Silicon. The Silicon–Sulfur Bond

*Sir:*

General interest in the chemistry of the silicon–sulfur bond, coupled with the great lack of mechanistic information concerning reactions of this bond[1] plus our previous studies of the dynamic stereochemistry of the silicon–oxygen bond,[2] have made it important to study the stereochemistry of the silicon–sulfur bond.

We wish to report: (a) the first syntheses of optically active $R_3Si^*S$ compounds, in which $R_3Si^*$ is α-naphthylphenylmethylsilyl, α-NpPhMeSi*; (b) a high degree of stereospecificity for reactions of the silicon–sulfur bond with various reagents; (c) some interesting changes

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(1) For previous work in the field of organosilicon sulfur chemistry see: C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp 333–338; V. Bažant and V. Chvalovský, "Organosilicon Compounds," Vol. 1, Academic Press Inc., New York, N. Y., 1965, pp 72–75; A. Haas, *Angew. Chem.*, **77**, 1066 (1965); H. J. Emeléus and M. Onyszchuk, *J. Chem. Soc.*, 604 (1958); E. W. Abel, *ibid.*, 4406 (1960); H. Gilman and G. Lichtenwalter, *J. Org. Chem.*, **25**, 1064 (1960); E. W. Abel, *J. Chem. Soc.*, 4933 (1961); L. Birkofer, A. Ritter, and H. Goller, *Ber.*, **96**, 3289 (1963); E. W. Abel, D. A. Armitage, and R. P. Bush, *J. Chem. Soc.*, 2455 (1964); E. W. Abel, D. A. Armitage, and R. P. Bush, *ibid.*, 3045 (1965); E. W. Abel, D. A. Armitage, and R. P. Bush, *ibid.*, 7098 (1965); K. A. Hooton and A. L. Allred, *Inorg. Chem.*, **4**, 671 (1965); E. W. Abel, D. A. Armitage, and D. B. Brady, *J. Organometal. Chem.* (Amsterdam), **5**, 130 (1966); M. Rimpler, *Ber.*, **99**, 1523 (1966); M. Rimpler, *ibid.*, **99**, 1528 (1966).

(2) (a) L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Am. Chem. Soc.*, **86**, 3276 (1964); (b) L. H. Sommer, G. A. Parker, and C. L. Frye, *ibid.*, **86**, 3280 (1964).

in dynamic stereochemistry engendered by the replacement of oxygen in $R_3Si^*O$ by sulfur; and (d) assignment of absolute configuration to several $R_3Si^*S$ compounds.

Reaction of $(-)$-$R_3Si^*Cl$ with $H_2S$ and $Et_3N$ in pentane solvent gave crystalline $(+)$-1,3-di-$\alpha$-naphthyl-1,3-diphenyl-1,3-dimethyldisilthiane, $R_3Si^*SSi^*R_3$, mp 115–116°, in 40–50% yields. 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,[2a] indicating high stereospecificity for breaking of the first silicon–sulfur bond in I. The other product, formed without breaking of the second silicon–sulfur bond, is $(+)$-diethylammonium $\alpha$-naphthylphenylmethylsilyl mercaptide (II). This product conveniently precipitates from the reaction mixture as fluffy, white crystals, mp 105–130° dec.

$$\begin{aligned}&\underset{[\alpha]_D\ +34^\circ}{2(+)\text{-}R_3Si^*H} \xrightarrow[a]{Cl_2} \underset{[\alpha]_D\ -6.3^\circ}{2(-)\text{-}R_3Si^*Cl} \xrightarrow[b]{H_2S,\ Et_3N} \underset{\text{I},\ [\alpha]_D\ +101^\circ}{(+)\text{-}R_3Si^*SSi^*R_3}\\ &\underset{\text{II},\ [\alpha]_D\ +52^\circ}{(+)\text{-}R_3Si^*S^-Et_2NH_2^+} + \underset{[\alpha]_D\ +17^\circ}{(+)\text{-}R_3Si^*OCH_3} \xleftarrow[c]{CH_3OH,\ Et_2NH} \qquad (1)\end{aligned}$$

Previous assignment[3] of the $(+)$-$R_3Si^*H$ configuration to $(+)$-$R_3Si^*OCH_3$ shows over-all retention of configuration for the conversion of $R_3Si^*H$ to $R_3Si^*$-$OCH_3$ in reaction sequence 1, and since reaction 1a is known to proceed with retention, reactions 1b and 1c must be either both inversions or both retentions. Predominant inversion stereochemistry for the reactions of $R_3Si^*Cl$ with a wide variety of nucleophiles, including water and alcohols and alcoholate ions,[4] makes the choice of inversion for (1b), and hence also for (1c), seem most reasonable. Studies of the lithium aluminum hydride reduction of the disilthiane and of $R_3Si^*SH$ reported below provide further evidence for correct assignment of inversion stereochemistry to (1b) and (1c).

Formation of II from I does not affect the second asymmetric silicon and obviously proceeds with retention of configuration.

Hydrolysis of the $(+)$-disilthiane under conditions similar to those used for the methanolysis gave $(+)$-$R_3Si^*OH$ which has the same configuration as $(+)$-$R_3Si^*OCH_3$.[2a] The product silanol had high optical purity and was formed with inversion of configuration.

$$\underset{[\alpha]_D\ +101^\circ}{(+)\text{-}R_3Si^*SSi^*R_3} \xrightarrow[Et_2O]{H_2O,\ Et_2NH} \underset{[\alpha]_D\ +19^\circ}{(+)\text{-}R_3Si^*OH} + \underset{[\alpha]_D\ +49^\circ}{(+)\text{-}R_3Si^*S^-Et_2NH_2^+} \qquad (2)$$

Addition of 1 equiv of HCl–benzene to a benzene solution of the $(+)$-amine salt II resulted in the precipitation of $Et_2NH_2^+Cl^-$, and removal of solvent gave a material crystallizable from pentane and identified as $(+)$-$\alpha$-naphthylphenylmethylsilylthiol ($(+)$-$R_3Si^*SH$, III), mp 63–64°.

$$\underset{[\alpha]_D\ +52^\circ}{(+)\text{-}R_3Si^*S^-Et_2NH_2^+} + HCl \xrightarrow{\text{benzene}} \underset{\text{III},\ [\alpha]_D\ +26^\circ}{(+)\text{-}R_3Si^*SH} + Et_2NH_2^+Cl^- \qquad (3)$$

Reaction of the $(+)$-amine salt II with methyl iodide in pentane–ether gave $(+)$-$\alpha$-naphthylphenylmethyl(methylthio)silane ($(+)$-$R_3Si^*SCH_3$, IV), mp 57–59°, after filtration from precipitated $Et_2NH_2^+I^-$ and removal of solvent.

$$\underset{\text{II},\ [\alpha]_D\ +52^\circ}{(+)\text{-}R_3Si^*S^-Et_2NH_2^+} + CH_3I \xrightarrow{\text{pentane–ether}} \underset{\text{IV},\ [\alpha]_D\ +12^\circ}{(+)\text{-}R_3Si^*SCH_3} + Et_2NH_2^+I^- \qquad (4)$$

Since 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 gives the configurational correlations with reference to the parent $(+)$-$R_3Si^*H$, together with specific rotations. All of the new compounds gave satisfactory analyses and infrared spectra.

**Table I.** Enantiomers Having the $(+)$-$R_3Si^*H$ Configuration[a]

| Compound | [α[D], deg (solvent) | Concn, g/100 ml |
|---|---|---|
| $(-)$-$R_3Si^*SSi^*R_3$ | −101 (hexane) | 0.5 |
| $(-)$-$R_3Si^*S^-Et_2NH_2^+$ | −52 (benzene) | 0.7 |
| $(-)$-$R_3Si^*SH$ | −26 (pentane) | 1.0 |
| $(-)$-$R_3Si^*SCH_3$ | −12 (pentane) | 2.0 |

[a] The absolute configuration of $(+)$-$R_3Si^*H$ has been determined.[3]

Further support for assignment of the $(+)$-$R_3Si^*H$ configuration to the levorotatory enantiomers listed in Table I was obtained by comparing the lithium aluminum hydride reductions of $(+)$-$R_3Si^*SSi^*R_3$ and $(+)$-$R_3Si^*SH$. Reduction of the $(+)$-disilthiane with excess $LiAlH_4$ in ether solvent *at room temperature* gave $(+)$-$R_3Si^*H$ in no more than 50% yield. The second silicon–sulfur bond, as indicated in reaction 5a, most probably is present in a mercaptide salt whose structure is approximated by V. On work-up of V, $(+)$-$R_3Si^*SH$ was formed and was recovered as the $(+)$-diethylammonium mercaptide.

$$\underset{\text{I},\ [\alpha]_D\ +101^\circ}{(+)\text{-}R_3Si^*SSi^*R_3} + LiAlH_4 \xrightarrow[\substack{Et_2O\\ \text{inversion}}]{22^\circ,\ 30\ \text{min}} \underset{[\alpha]_D\ +34^\circ}{(+)\text{-}R_3Si^*H} + \underset{\text{V}}{[R_3Si^*S^-(LiAlH_3)^+]} \qquad (5a)$$

$$\text{V} \xrightarrow{\text{HCl work-up}} \underset{\text{in product mixture}}{[(+)\text{-}R_3Si^*SH]} \xrightarrow{Et_2H} \underset{[\alpha]_D\ +51^\circ}{(+)\text{-}R_3Si^*S^-Et_2NH_2^+} \qquad (5b)$$

Structure V was independently generated by a mixture of $LiAlH_4$ and the $(+)$-silylthiol (III) at −70°, and found, in accord with reaction 5a, to be inert at room temperature. However, when heated at 85° for 24 hr V gave $(-)$-$R_3Si^*H$.

$$\underset{[\alpha]_D\ +26^\circ\ (\text{III})}{(+)\text{-}R_3Si^*SH} + LiAlH_4 \xrightarrow[-H_2]{-70^\circ} \xrightarrow[24\ \text{hr}]{\text{room temp}} \text{V} \xrightarrow[\substack{Et_2O\text{–}Bu_2O\\ \text{retention}}]{85^\circ,\ 24\ \text{hr}} \underset{[\alpha]_D\ -30^\circ}{(-)\text{-}R_3Si^*H} \qquad (6)$$

Since $(+)$-$R_3Si^*SSi^*R_3$ and $(+)$-$R_3Si^*SH$ have the same configuration at all three silicon atoms, and since

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

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

the former gives (+)-$R_3Si^*H$ by reduction and the latter gives (−)-$R_3Si^*H$, it follows that opposite stereochemical paths obtain for formation of $R_3Si^*H$ in reactions 5a and 6. Use of leaving group reasoning (see below) clearly favors assignment of an inversion stereochemistry to the formation of (+)-$R_3Si^*H$ in reaction 5a and, in turn, reinforces assignment of the (+)-$R_3Si^*H$ configuration to the levoratatory enantiomers in Table I.

Thus, reaction 5a involves inversion and reaction 6 involves retention of configuration. The results for these two reactions were combined experimentally in a total reduction of the (+)-disilthiane, in which reaction 5a was directly followed by heating at 85°, and *racemic* $R_3Si^*H$ was obtained in 95% yield.

Reduction of the (+)-amine salt II was complicated by its low solubility in ether solvent, but when brought into contact with $LiAlH_4$ it went rapidly into solution, and upon heating at 85° yielded (−)-$R_3Si^*H$, for which retention of configuration follows from the assigned configurational relationships.

$$\underset{[\alpha]\text{D} +52°\ (\text{II})}{(+)\text{-}R_3Si^*S^-Et_2NH_2^+} + LiAlH_4 \xrightarrow[\text{retention}]{85°} \underset{[\alpha]\text{D} -21°}{(-)\text{-}R_3Si^*H} \qquad (7)$$

Reaction of the (+)-methylthiosilane (IV) with $LiAlH_4$ in refluxing $Et_2O$ gave (+)-$R_3Si^*H$, with inversion of configuration.

$$\underset{\text{IV, } [\alpha]\text{D} +12°}{(+)\text{-}R_3Si^*SCH_3} + LiAlH_4 \xrightarrow[\text{inversion}]{Et_2O\text{ reflux}} \underset{[\alpha]\text{D} +29°}{(+)\text{-}R_3Si^*H} \qquad (8)$$

Methanolysis and hydrolysis of the disilthiane I (reactions 1c and 2) are complete in minutes at room temperature, in comparison to optically active $R_3Si^*$-$OSi^*R_3$ which is unchanged after many hours under the same conditions. Reduction of the first silicon–sulfur bond in I (reaction 5a) is complete in 30 min at room temperature, whereas attempted reduction of $R_3Si^*OSi^*R_3$ by heating with $LiAlH_4$ at 45° overnight gave only a trace of $R_3Si^*H$.[2a,5] Thus it is clear that $RS^-$ is a better leaving group than its oxygen analog, $RO^-$, with nucleophilic reagents.[6] Also, reactions 1c, 2, 5a, 6, and 7 reveal the (not unexpected) fact that $RS^-$ is a better leaving group than $S^{2-}$.

The stereochemical consequences of the above leaving group relationships are of considerable interest. Thus, *inversion* in reaction 8 is in sharp contrast to the highly stereospecific reduction of $R_3Si^*OCH_3$ with *retention* of configuration by $LiAlH_4$ in ether solvent.[2a] *Inversion* for the reduction of the first Si*–S bond in the disilthiane is also in sharp contrast to reduction of both Si*–O bonds with *retention* of configuration in the reaction of $R_3Si^*OSi^*R_3$ with $LiAlH_4$ at elevated temperature.[2a] Furthermore, other reactions of $R_3Si^*OCH_3$ and $R_3Si^*OSi^*R_3$ are known to proceed with *retention* of configuration,[2a] unlike the situation for reactions of $R_3Si^*$–SY which usually proceed with *inversion* of configuration. The present stereochemical studies of the silicon–sulfur bond provide additional evidence for the concept of inversion of configuration being favored by better leaving groups, whereas retention of configuration is common for poorer leaving groups in nonpolar solvents.[7] A clear case of operation of this principle is provided in the present work by *inversion* for reaction 5a ($RS^-$ leaving group) and retention in reaction 7 ($S^{2-}$ leaving group).[8,9]

**Acknowledgment.** We thank Dow Corning Corporation for continued generous support.

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[5] Unpublished work of L. H. Sommer and C. L. Frye. Reduction of $R_3Si^*OSi^*R_3$ to $R_3Si^*H$ was accomplished in 42% yield after heating at 110° for 3 days and at 143° for 8 hr. See ref 2a.

[6] Increased reactivity of the sulfur compounds with nucelophilic reagents, relative to the rates of their oxygen analogs, is in accord with previous conclusions of increased reactivity of $R_3SiX$ with smaller values of p$K_a$ for HX. See ref 4, Chapter 8.

[7] See ref 4, Chapters 3 and 11. For example, the change from $RCO_2^-$ to $RO^-$ as a leaving group frequently results in a change from inversion to retention of configuration.

[8] The actual leaving group may approximate $H_3AlS^-$, but inductive electron release from aluminum to sulfur should still make this complex leaving group poorer than $RS^-$.

[9] Formation of $Et_3SiSSiEt_3$ from $Et_3SiCl$ and $H_2S$ has been reported by G. Champetier, Y. Etiennes, and R. Kullman, *Compt. Rend.*, **234,** 1985 (1952). Compound II is the first example of an amine salt of $R_3SiSH$.

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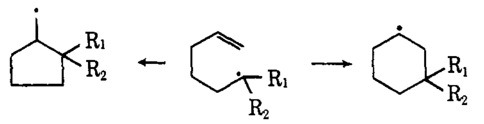
## Radical Cyclizations in the Reaction of Trialkyltin Hydrides with Alkenyl Halides[1]

*Sir:*

The cyclization of 5-hexenyl radicals has been the subject of several recent papers and is of considerable interest since the direction of ring closure varies strikingly with changes in radical structure.



(1)

Thus with highly substituted radicals ($R_1$ = COOR, $R_2$ = CN) Julia[2] reports chiefly formation of cyclohexyl derivatives, while the simple 5-hexenyl radical cyclizes almost exclusively to the cyclopentylmethyl radical.[3–5] Five-membered-ring products are also preferred in intermediate cases, as in the addition of a number of radicals to 1,6-heptadiene, diallyl ether, and ethyl diallylacetate.[6,7]

The five-membered-ring closure is surprising since it is energetically unfavorable and contrary to the usual direction of radical addition, and we are investigating it in more detail. For this purpose we find that the reaction of organic halides with tributyltin hydride, developed by Kuivila,[8] provides a convenient means of generating a variety of radicals and that the cyclization in many cases competes favorably with reaction of the uncyclized radical with the hydride. Some preliminary

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[1] Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

[2] M. Julia and Maumy, *Bull. Soc. Chim. France*, 434 (1966), gives a good summary of earlier work.

[3] R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85,** 3483 (1963).

[4] C. Walling and M. S. Pearson, *ibid.*, **86,** 2262 (1964).

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[6] N. O. Brace, *J. Am. Chem. Soc.*, **86,** 523 (1964).

[7] J. I. G. Cadogan, *Chem. Ind.* (London), 753 (1964).

[8] L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86,** 3047 (1964).