the HCl adduct will yield the same silyl-stabilized carbonium ion which can go on to product.

Bridging trimethylsilyl groups which stabilize a β-carbonium ion center have been observed. Reisolation of unreacted starting material from the partial solvolysis of 2-bromo-2,2-dideuterio-1-trimethylsilylethane yields 2-bromo-1-trimethylsilylethane in which the deuterium has been extensively scrambled between C_1 and C_2.[11]

The reaction of trifluoromethanesulfonic acid with *trans*-β-trimethylsilylstyrene to yield styrene supports this third pathway. The inability of the trifluoromethanesulfonate anion to function as a nucleophile to carbon precludes the operation of a cis addition followed by trans elimination mechanism in this case. However, attack by the trifluoromethanesulfonate anion on silicon leading to formation of trimethylsilyl trifluoromethanesulfonate can occur.[13]

Further studies to determine the scope of this reaction are in progress.

Acknowledgments. This work was supported in part by a grant from the Air Force Office of Scientific Research (AFOSR-73-2424). We also thank the mass spectrometry laboratory of J. P. L. for their help. Discussions with Professor T. G. Traylor were most helpful.

[13] Analogous distillable liquid trialkylsilyl perchlorates apparently having a covalent silicon–oxygen bond have been reported: U. Wannagat and W. Liehr, *Angew. Chem.*, 69, 783 (1957).

[14] National Science Foundation Trainee, 1970–1973.

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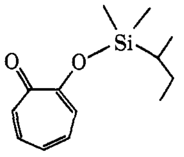
Stereochemical Studies of Degenerate Silyl Rearrangements. Stereospecificity of the Tropolone and Acetylacetone Trialkysilyl Ether Rearrangements

Sir:

A number of degenerate rearrangements of trimethylsilyl groups bonded to electronegative elements have been discovered in recent years.[1] We report here the discovery of a new rearrangement of this type (tropolone silyl ether) and the stereochemistry at silicon of this reaction and of the trialkylsilyl acetylacetonate[1a] (*trans*-4-trialkylsiloxypent-3-en-2-one (**2**)) rearrangement.

Silylation of tropolone with 2-butyldimethylchlorosilane[2]–triethylamine gave 2-(2-butyldimethylsiloxy)-cyclohepta-2,4,6-trienone (**1**) (bp 90° (0.2 mm); nmr $\delta^{\mathrm{TMS}}_{\mathrm{CDCl_3}}$ 0.28 (s, 6 H), 0.8–1.8 (m, 9 H), 6.6–7.3 (m, 5 H); ir $\nu_{\mathrm{CHCl_3}}$ 1620, 1590, 1575 $\mathrm{cm^{-1}}$). The carbonyl frequency is somewhat shifted from that of tropone (1638 $\mathrm{cm^{-1}}$)[3] and tropolone methyl ether (1629 $\mathrm{cm^{-1}}$), suggesting a small interaction between silicon and the carbonyl oxygen in the ground state.



1

The proton nmr spectrum of **1** is essentially independent of temperature down to −75°. The ^{13}C nmr spectrum[4] at 0° shows only four resonances in the low-field region ($\delta^{\mathrm{TMS}}_{\mathrm{CDCl_3}}$ 127.9 (C-5), 128.4, 135.0, 171.8 (C-1,2)) instead of the seven olefinic and carbonyl peaks expected for the static structure (*cf.* tropolone, $\delta^{\mathrm{TMS}}_{\mathrm{CDCl_3}}$ 123.6, 127.9, 137.2, 171.4 (C-1,2)). Accidental coincidence of the various chemical shifts can be ruled out, since the ^{13}C resonances of tropolone methyl ether ($\delta^{\mathrm{TMS}}_{\mathrm{CDCl_3}}$ 56.3 ($\mathrm{OCH_3}$), 112.5, 128.9, 132.8, 136.6, 136.8, 165.5 (C-2), 180.5 (C-1)) are well separated, in particular, the two carbons bonded to oxygen. We conclude that degenerate silyl migration is ocurring rapidly on the nmr time scale in **1**. The cmr spectrum shows some broadening of the lowest field resonance (C-1,2) beginning at −50° (Figure 1). The C–O carbons broaden at the highest temperature since they probably have the largest chemical-shift separation in the static structure. Carbon-5 is symmetrically situated and should not exhibit any temperature dependence, as is, indeed, observed. At the lowest temperature attained (−75°), no peak has reached coalescence.

A rough estimate of activation energy ($k = 1.9 \times 10^4\ \mathrm{sec^{-1}}$ at −60°, $\Delta F^{\ddagger} = 8.2$ kcal/mol) for the silyl shift can be made from the broadening of C-1,2 observed between −50 and −70° assuming that the chemical-shift difference between C-1 and C-2 of **1** is the same as in tropolone methyl ether (388 Hz).

The upfield portion of the cmr spectrum of **1** shows the expected butyl resonances (δ^{TMS} (0°) 12.98 ($\mathrm{CH_3}$), 12.90 ($\mathrm{CH_3}$), 23.78, 23.87), and two peaks for the diastereotopic Si–$\mathrm{CH_3}$ carbons (−1.37, −1.42). The resonances for the geminal dimethyl carbons move closer together at higher temperature and above 35° can no longer be resolved. The observation of separate Si–$\mathrm{CH_3}$ peaks in the rapidly rearranging system demonstrates that the silyl shift is occurring with retention of configuration at silicon, since any migration with inversion or racemization would interchange the methyl environments. Inversion at silicon must have a rate constant smaller than 0.97 $\mathrm{sec^{-1}}$ at 35° ($\Delta F^{\ddagger} \geq 18.1$ kcal/mol). A rough extrapolation[5] of the rate of isomerization to 35° gives a rate constant of $1.1 \times 10^7\ \mathrm{sec^{-1}}$, so that the stereospecificity of the internal displacement is at least one part in 10^7.

We have also prepared 2-butyldimethylsilyl acetyacetonate (19:81 mixture of **2** and **3**) by silylation of acetylacetone with 2-butyldimethylchlorosilane.[2] Highly accurate rate measurement for the degenerate isomerization of **2** is not possible because resonances

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[1] (a) T. J. Pinnavaia, W. T. Collins, and J. J. Howe, *J. Amer. Chem. Soc.*, 92, 4544 (1970); (b) D. H. O'Brien and C.-P. Hrung, *J. Organometal. Chem.*, 27, 185 (1971); (c) O. J. Scherer and P. Hornig, *Chem. Ber.*, 101, 2533 (1968); (d) N. Wiberg and H. J. Pracht, *ibid.*, 105, 1388 (1972); (e) R. West and B. Bichlmeier, *J. Amer. Chem. Soc.*, 94, 1649 (1972).

[2] Treatment of trichlorosilane successively with 2-butylmagnesium bromide (1 equiv) and methylmagnesium iodide (2 equiv) gave 2-butyldimethylsilane (44%), which was chlorinated with $\mathrm{Cl_2}$ in pentane.

[3] W. von E. Doering and F. L. Detert, *J. Amer. Chem. Soc.*, 73, 876 (1951).

[4] Varian XL-100 system in Fourier transform mode at 25.16 MHz with noise-modulated proton decoupling. Low-temperature spectra were measured in $\mathrm{CDCl_3}$ and high-temperature spectra in $\mathrm{C_6H_5COCD_3}$ as solvent.

[5] It is assumed that $\Delta S^{\ddagger} = 0$ eu. A value of $\Delta S^{\ddagger} = -0.8$ eu has been reported for the trimethylsilyl acetylacetonate rearrangement,[1a] and values ranging from −1.2 to −7.2 eu for various silyltriazene rearrangements.[1d] The extrapolated rate constant for silyl shift in **1** becomes $2.4 \times 10^6\ \mathrm{sec^{-1}}$ at 35° if $\Delta S^{\ddagger} = -10$ eu.

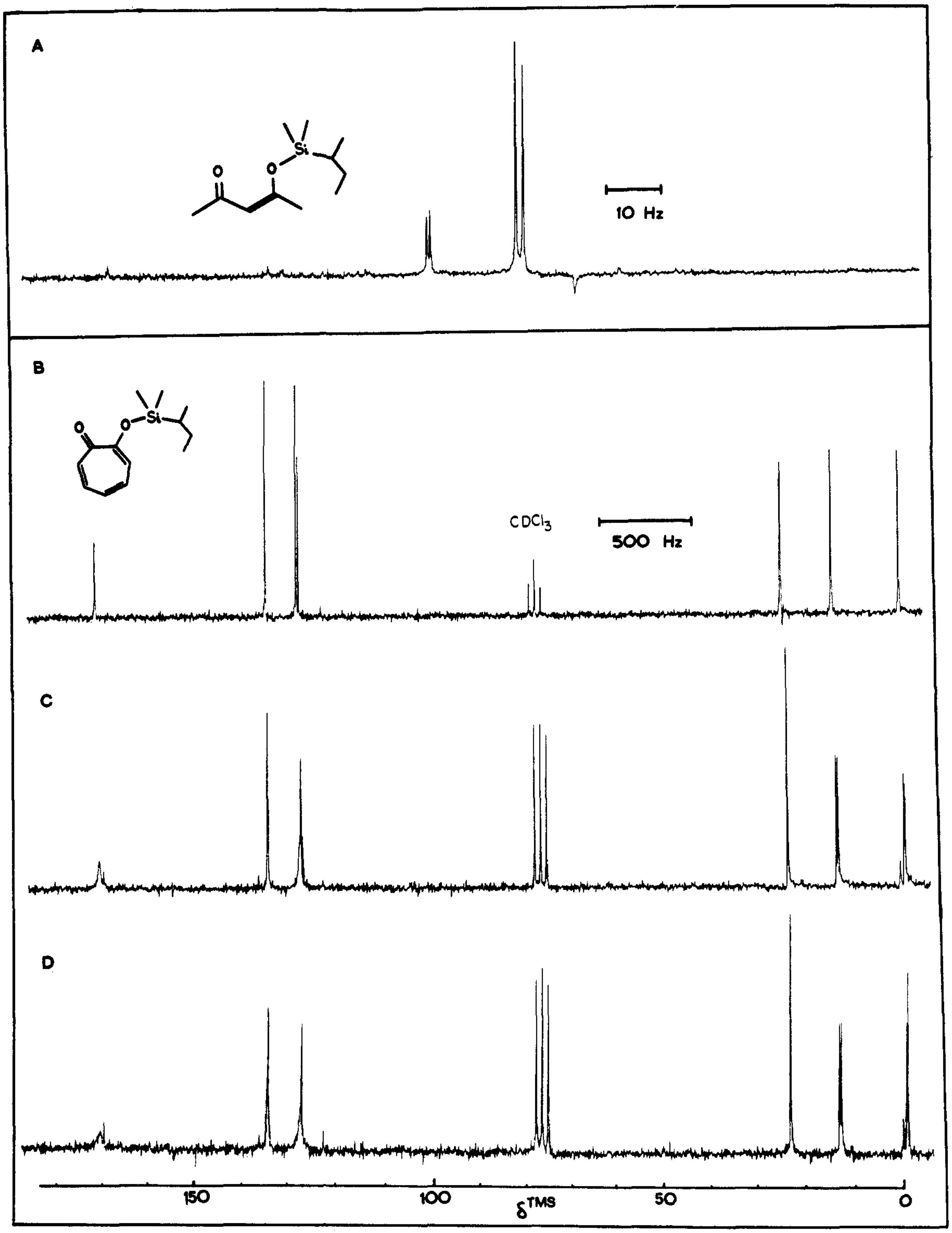
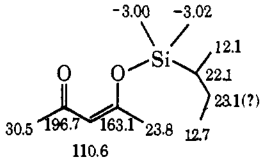


Figure 1. ^{13}C nmr spectra:[4] (A) narrow sweep spectrum of the Si(CH$_3$)$_2$ resonances of **2** and **3** at 35°; (B–D) wide sweep spectra of **1** at 0, −60, and −70°, respectively. The small peaks at δ 0.3, 123, 137, and 171 in C and D are due to impurities caused by a small amount of hydrolysis.

Chart I. ^{13}C Chemical Shifts of **2** and **3** at −20° ($\delta^{\mathrm{TMS}}_{\mathrm{CDCl_3}}$)



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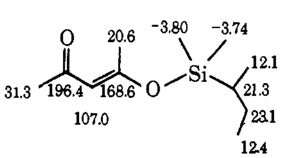


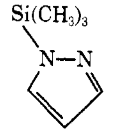
3

of **2** in the pmr spectrum are partially obscured by those of the major isomer **3**, but we find $\Delta F^{\ddagger} = 15.4$ kcal/mol by line-shape analysis between −18 and 25°. Pinnavaia, Collins, and Howe[1a] found $\Delta F^{\ddagger} = 13.4$ kcal/mol and $\Delta S^{\ddagger} = -0.8 \pm 2.5$ eu at 25° for the trimethylsilyl derivative.

The variable temperature cmr spectrum[4] (Chart I) of the mixture of **2** and **3** is fully consistent with the conclusions made by Pinnavaia. Only the acetylacetone methyls and C–O carbons exhibit broadening and coalescence between −20 and 100°.[4] Both isomers have diastereotopic Si(CH$_3$)$_2$ resonances (Figure 1A), and the nonequivalent methyls of **2** could be resolved up to 150° ($k_{\mathrm{inv}} \leq 1.55\ \mathrm{sec}^{-1}$, $\Delta F^{\ddagger} \geq 24.6$ kcal/mol). Extrapolation of the rate of silyl migration[5] to 150° gives a stereospecificity of one part in 59,000, or 99.99998% retention.[5a]

It should be emphasized that for neither **1** nor **2** was a clear-cut coalescence of the $Si(CH_3)_2$ resonances observed. The chemical-shift difference is sufficiently small ($\approx$0.7 Hz at 25 MHz) that the distinction between coalescence and failure to resolve closely spaced peaks is difficult to make.

Although the degenerate silyl shifts in **1**, **2**, **4**,[1b] **5**,[1d] and **6**[1e] can be considered as [1,9], [1,5], [1,5], [1,3], and [1,2] sigmatropic rearrangements, respectively, the facility with which all of these reactions proceed suggests that they are best considered as internal nucleophilic displacements.[6] Orbital symmetry rules predict that the suprafacial migrations with retention of configuration at silicon in **5** and **6** are disallowed, yet these systems do not have unusually high barriers when compared with the symmetry-allowed reactions of **1**, **2**, and **4**.



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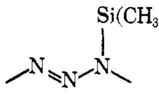
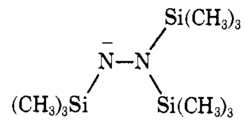
E_a = 24 kcal/mol



5

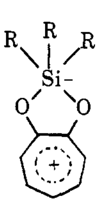
$\Delta F^{\ddagger}$ = 16.1 kcal/mol



6

$\Delta F^{\ddagger}$ = 10.9 kcal/mol

The extremely low barrier to rearrangement in **1** offers support for the suggestion[1a,7] of a pentacoordinate silicon intermediate in these reactions, since here the dipolar species is highly stabilized (**7**). However, neither in **1** nor in **2** can the two oxygens adopt diequatorial positions (*e.g.*, **8**) in the trigonal-bipyramidal intermediate, since this would result in inversion of configuration at silicon. Such an intermediate must have the six-membered ring (**9**) or five-membered ring (for **1**) in apical-equatorial positions, and the barrier for pseudorotation to an ee intermediate like **8** must be at least 9.2 kcal/mol for **2** and 9.9 kcal/mol for **1**.



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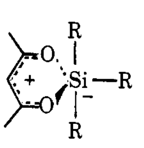

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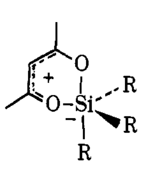

9

Intramolecular nucleophilic displacements at silicon for which the stereochemistry is known[8] have involved three- or four-membered cyclic transition states, and all have proceeded with predominant retention of configuration. Our results strongly suggest that intramolecular displacements involving five- and six-membered cyclic transition states also proceed with high retention, at least where both entering and leaving groups are electronegative elements. This offers support to the many suggestions in the literature[9] that intermolecular displacements at silicon proceeding with retention of configuration do so because interactions between entering and leaving groups result in a cyclic transition state.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for partial support of this research.

(5a) NOTE ADDED IN PROOF. I. K. Kusnezowa, K. Rühlmann, and E. Gründemann (*J. Organometal. Chem.*, **47**, 53 (1973)) have reported the preparation of optically active silyl acetylacetonates. If the observed optical activity is not entirely due to the *E* isomer (**3**, SiR_3 = Si(Ph)(Me)(α-Naph)) then their results also demonstrate silyl migration with retention of configuration at silicon in the *Z* isomer.

(6) The barrier to [1,3] migration in crotyltrimethylsilane is E_a = 47.7 kcal/mol: H. Kwart and J. Slutsky, *J. Amer. Chem. Soc.*, **94**, 2515 (1972).

(7) M. Gielen, C. Dehouk, H. Mokhtar-Jamai, and J. Topart, *Rev. Silicon, Germanium, Tin, Lead Compounds*, **1**, 1 (1972).

(8) (a) A. G. Brook, D. M. MacRae, and W. W. Limburg, *J. Amer. Chem. Soc.*, **89**, 5493 (1967); (b) A. G. Brook, C. M. Warner, and W. W. Limburg, *Can. J. Chem.*, **45**, 1231 (1967); A. G. Brook and J. D. Pascoe, *J. Amer. Chem. Soc.*, **93**, 6224 (1971); (c) J. F. Klebe, *ibid.*, **90**, 5246 (1968).

(9) (a) D. G. Anderson and D. E. Webster, *J. Chem. Soc. B*, 878 (1968); (b) L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Amer. Chem. Soc.*, **86**, 3276 (1964); (c) L. H. Sommer and J. D. Citron, *ibid.*, **89**, 5797 (1967); (d) L. H. Sommer and J. E. Lyons, *ibid.*, **91**, 7061 (1969).

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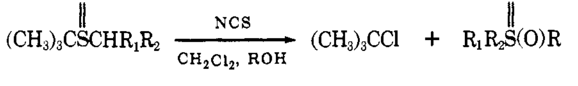
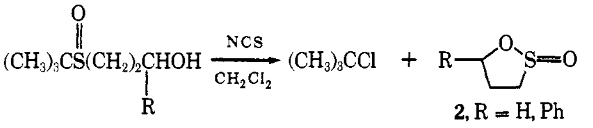
β-Sultines. Intermediates in a Sulfur Analog of the Wittig Olefin Synthesis

Sir:

We have recently reported that *tert*-butyl alkyl or aryl sulfoxides undergo carbon–sulfur bond cleavage upon treatment with positive halogen species such as *N*-bromo- or *N*-chlorosuccinimide.[1] When the cleavage reactions were carried out in the presence of alcohols, the products were sulfinic esters and *tert*-butyl halides (eq 1). Incorporation of the hydroxyl group into the γ or δ position of the alkyl group resulted in the formation of γ- or δ-sultines,[1,2] *e.g.*, **1** → **2** (85%).

 (1)

$$(CH_3)_3C\overset{O}{\overset{\|}{S}}CHR_1R_2 \xrightarrow[CH_2Cl_2,\ ROH]{NCS} (CH_3)_3CCl + R_1R_2\overset{O}{\overset{\|}{S}}(O)R \quad (1)$$

 (2)

1, R = H, Ph

2, R = H, Ph

We have found that β-hydroxy sulfoxides (**3**) also react with NBS, NCS, or SO_2Cl_2 in CH_2Cl_2 or CCl_4 at

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(1) F. Jung and T. Durst, *J. Chem. Soc., Chem. Commun.*, 4 (1973).

(2) The synthesis and properties of very few γ- and δ-sultines have been described; *cf.* (a) D. N. Harpp and J. G. Gleason, *Tetrahedron Lett.*, 1447 (1969); *J. Org. Chem.*, **36**, 1314 (1971); (b) J. F. King, P. de Mayo, C. L. McIntosh, K. Piers, and D. J. H. Smith, *Can. J. Chem.*, **48**, 3704 (1970); (c) R. M. Dodson, P. D. Hammen, and R. A. Davis, *J. Org. Chem.*, **36**, 2693 (1971); (d) D. C. Dittmer, R. S. Henion, and N. Takashina, *ibid.*, **34**, 1310 (1969). Because of the accessibility of a variety of compounds of the type **1**, the above route, eq 2, leads to sultines of varying ring size and substitution. Work in this area will be reported shortly.