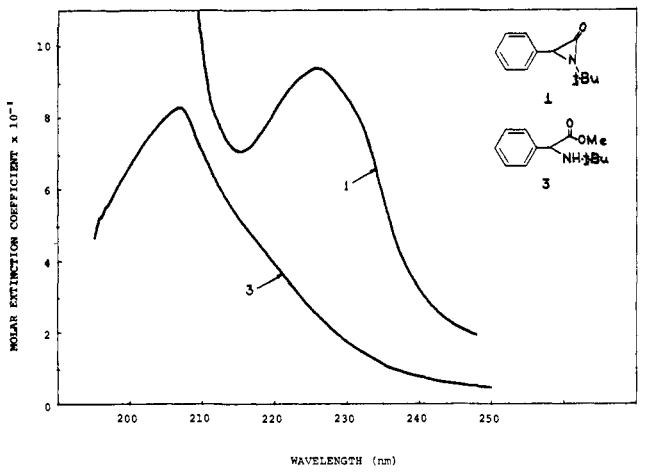


Figure 1. Uv spectra of 1-*tert*-butyl-3-phenylaziridinone (**1**) and methyl 2-*tert*-butylamino-2-phenylacetate (**3**).

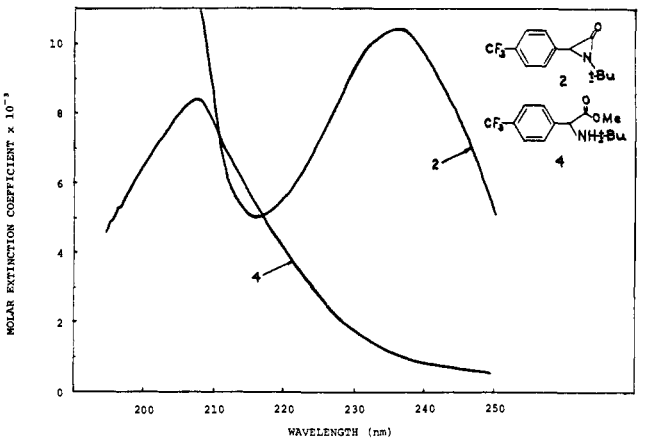
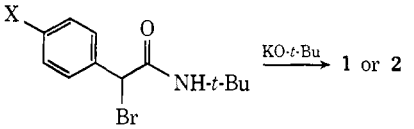


Figure 2. Uv spectra of 1-*tert*-butyl-3-(*p*-trifluoromethyl)phenylaziridinone (**2**) and methyl 2-*tert*-butylamino-2-(*p*-trifluoromethyl)-phenylacetate (**4**).

lactams.[6] The corresponding *N*-*tert*-butyl-2-bromophenylacetamide **5** or **6**[7] (1 equiv) is treated with po-

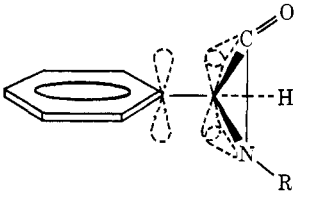


5, X = H
6, X = CF_3

tassium *tert*-butoxide (1 equiv) in diethyl ether for 30 min at a reaction temperature maintained between −40 and −50°. The reaction mixture is removed through a syphon under nitrogen pressure and filtered into a flask cooled in Dry Ice. After removal of the solvents under reduced pressure at 0°, the residue, a yellow oil, is dissolved in pentane and cooled in Dry Ice, and the precipitate is separated by centrifugation. Concentration of the supernatant liquid followed by distillation in a molecular still at 50–60° (0.003 mm) gives the α-lactams **1** and **2** in 23–35% yield.[8,9]

The open-chain analogs **3** and **4** are obtained by treating a stirred pentane solution of the corresponding α-lactam (1 equiv) with sodium methoxide (3 equiv) for 3 hr. Pure amino esters are isolated following aqueous work-up and preparative gas chromatography.[10]

The bathochromic shift observed in the present study presumably arises through a conjugative interaction of the aromatic π system with the α-lactam ring bonds similar to that illustrated, although experiments with phenylcyclopropyl analogs indicate a specific geometry is not necessary.[5] The trifluoromethyl group of **2** causes an increased and intensified bathochromic shift as expected for a para electron-withdrawing substituent. In general, substituents β to the aromatic ring exhibit no observable effect on the ultraviolet spectrum which appears to be the case for the carbonyl group and the nitrogen atom of the α-lactam ring since the absorption maxima of **1** is very similar to that of phenylcyclopropane (λ_{max} (pentane) 226 nm (log ε 3.9)).



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Reaction of Deuterium Chloride with *cis*- and *trans*-β-Trimethylsilylstyrene

Sir:

While the reactions of aryltrimethylsilanes with electrophiles have been extensively studied,[1] the reactions of vinylsilanes with electrophiles have been examined in much less detail.[2] The reaction of β-trimethylsilylstyrene with acid was reported to yield styrene almost 20 years ago.[3] We have been concerned with the mechanism of this reaction since we have found that it possesses an unusually high degree of stereospecificity for what must be a complex ionic reaction. Specifically we find that *trans*-β-trimethylsilylstyrene[4] reacts with either DCl or DBr in dry acetonitrile at reflux to yield virtually only *trans*-β-deuteriostyrene. Similarly *cis*-β-trimethylsilylstyrene[4] yields equally pure *cis*-β-deuteriostyrene.

(6) J. C. Sheehan and J. H. Beeson, *J. Amer. Chem. Soc.*, 89, 362 (1967).
(7) The starting amides **6** and **7** were prepared by the procedure described in ref 6.
(8) The spectroscopic yield of **2** in the reaction solution was 64.5% (±6%) based on a plot of infrared absorbances *vs.* known concentrations of **2**.
(9) The structures of the new compounds **2**, **3**, **4**, and **6** are consistent with elemental analyses, mass spectra, and nmr and infrared spectra.
(10) 32 cm × 0.4 cm 20% Silicone-200 on Chromosorb P at 155°.

(1) C. Eaborn and R. W. Bott, "Organometallic Compounds of the Group IV Elements," Vol. I, A. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, Chapter 2, pp 407–435.
(2) C. Eaborn and R. W. Bott in ref 1, pp 392–395.
(3) L. H. Sommer, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 76, 1613 (1954).
(4) D. Seyferth, L. G. Vaughan, and R. Suzuki, *J. Organometal. Chem.*, 1, 437 (1964).

The stereochemical purity of the products was determined by nmr on a Varian HA-100 (Figure 1), while the deuterium content was determined by mass spectrometry on an AEI MS-902 at an ionizing voltage below 10 eV, conditions under which styrene does not fragment to a P − 1 ion permitting easy determination of the per cent deuteration.[5] The small amount (less than 4% in each case) of hydrogen observed by nmr at the deuterium labeled position corresponds within 1% with the amount of nondeuterated material as determined by mass spectrometry.

Two mechanisms can be advanced to explain these results. The first would have a four-center transition state. Formation of the new carbon–hydrogen bond and the new silicon–chlorine bond would occur simultaneously with breaking of the carbon–silicon bond in the starting material. While this mechanism is economical, the following evidence does not favor it. β-Trimethylsilyl-*p*-methylstyrene reacts at least six–seven times faster with HCl than does β-trimethylsilylstyrene indicating that significant positive charge is developed at the benzylic carbon in the transition state. Certainly the remote phenyl ring would not be expected to have such an effect on a four-center transition state in which bond making and bond breaking were simultaneous.

A second mechanism which could explain the stereochemistry would involve cis addition of HCl to the carbon–carbon double bond of the styrene system followed by trans elimination of trimethylchlorosilane. There is precedent for both of these processes. Dewar and Fahey have shown that DBr adds 88% in a cis fashion to both *cis*- and *trans*-propenylbenzenes.[6] DBr also adds cis to acenaphthylene[7] and to indene.[8] Jarvie has shown that *erythro*-1,2-dibromopropyltrimethylsilane is unstable under solvolytic conditions. Trimethylbromosilane is lost in a trans fashion to yield *cis*-bromopropene of high stereochemical purity.[9]

Despite these analogies for cis addition of HCl followed by trans elimination of trimethylchlorosilane problems exist. The stereochemical purity of our product—>96%—would require a significantly higher stereoselectivity for cis addition of DBr or DCl than that observed by Dewar and Fahey. In addition, we have been unable to isolate an HCl or HBr adduct of *trans*-β-trimethylsilylstyrene. In fact the reaction of *trans*-β-trimethylsilylstyrene with 1.5 equiv of HCl in CS_2 at −100° for 1 hr results in total consumption of starting material and production of approximately a 1:1 ratio of styrene and α-chloroethylbenzene (the product of addition of HCl to styrene). Clearly, the reaction is not only stereospecific but also exceedingly fast. In an attempt to eliminate the HX adduct from the reaction pathway we have prepared 1-bromo-1-phenyl-2-trimethylsilylethane (the HBr adduct of β-trimethylsilylstyrene) by the NBS bromination of 1-phenyl-2-trimethylsilylethane[10] in CS_2. While it is stable in CS_2 at room temperature it decomposes in CS_2 in the presence of HCl even at −100° to yield styrene. Thus, if an HX adduct is formed it is unstable under the reaction conditions.

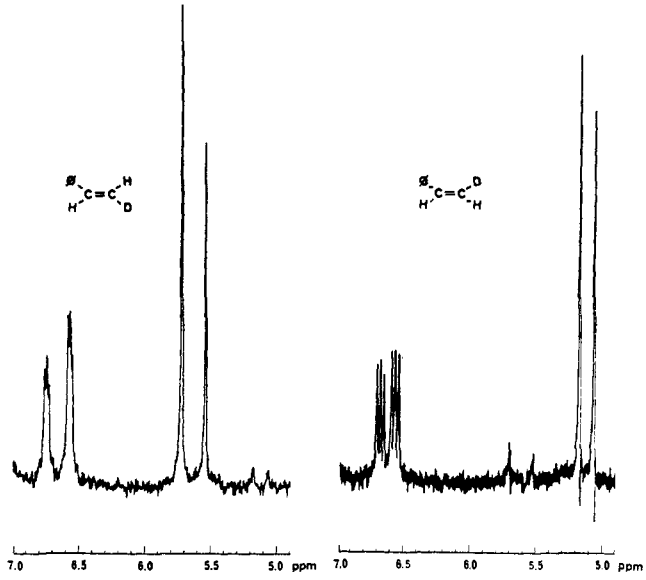
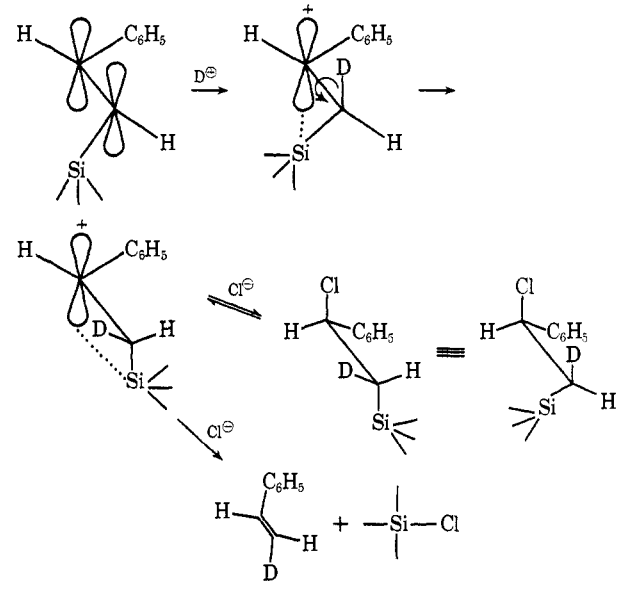


Figure 1. Nmr spectra of the vinyl region of *trans*- and *cis*-β-deuteriostyrenes.

A third mechanism may explain all the present data. Simultaneously with proton addition to the double bond, rotation occurs about the developing carbon–carbon single bond in the direction to permit the trimethylsilyl group to continuously stabilize the incipient benzylic carbonium ion center by bridging[11] or hyperconjugation[12] of the Si–C bond. Attack by the nucleophile, chloride anion, can now occur either on carbon of the benzylic carbonium ion to yield an HCl adduct or on silicon to yield the product (eq 1). Ionization of



(5) K. Biemann, "Mass Spectrometry–Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962; see Chapter 5 for treatment of data for deuterium-labeled compounds.
(6) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, 85, 3645 (1963).
(7) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, 85, 2704 (1963).
(8) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, 85, 2248 (1963).
(9) A. W. P. Jarvie, A. Holt, and J. Thompson, *J. Chem. Soc. B*, 852 (1969).
(10) H. Gilman and F. J. Marshall, *J. Amer. Chem. Soc.*, 71, 2066 (1949).
(11) (a) M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometal. Chem.*, 24, 301 (1970); (b) A. J. Bourne and A. W. P. Jarvie, *J. Organometal. Chem.*, 24, 335 (1970).
(12) T. G. Traylor, W. Hanstein, M. J. Berwin, N. A. Clinton, and R. S. Braun, *J. Amer. Chem. Soc.*, 93, 5715 (1971).

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.

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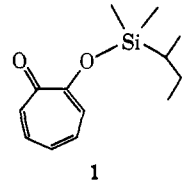
Stereochemical Studies of Degenerate Silyl Rearrangements. Stereospecificity of the Tropolone and Acetylacetone Trialkysilyl Ether Rearrangements

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)-cycloheptа-2,4,6-trienone (**1**) (bp 90° (0.2 mm); nmr $\delta^{TMS}_{CDCl_3}$ 0.28 (s, 6 H), 0.8–1.8 (m, 9 H), 6.6–7.3 (m, 5 H); ir ν_{CHCl_3} 1620, 1590, 1575 cm^{-1}). The carbonyl frequency is somewhat shifted from that of tropone (1638 cm^{-1})[3] and tropolone methyl ether (1629 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 ($\delta^{TMS}_{CDCl_3}$ 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, $\delta^{TMS}_{CDCl_3}$ 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 ($\delta^{TMS}_{CDCl_3}$ 56.3 (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 ($k = 1.9 \times 10^4$ 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 (CH_3), 12.90 (CH_3), 23.78, 23.87), and two peaks for the diastereotopic Si–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–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 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 1.1×10^7 sec^{-1}, so that the stereospecificity of the internal displacement is at least one part in 10^7.

We have also prepared 2-butyldimethylsilyl acetylacetonate (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

(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 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 $CDCl_3$ and high-temperature spectra in $C_6H_5COCD_3$ as solvent.

(5) It is assumed that $\Delta S^{\ddagger} = 0$ eu. A value of $\Delta S^{\ddagger} \approx -0.8$ 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 2.4×10^6 sec^{-1} at 35° if $\Delta S^{\ddagger} = -10$ eu.