

will provide the most fruitful means of studying the TL excitation mechanisms. In such systems, the TL spectra may contain dynamic features characteristic of the system under stress.

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Jeffrey I. Zink,* Wolfram Klimt

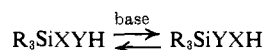
Department of Chemistry,¹³ University of California
Los Angeles, California 90024

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Base-Catalyzed Rearrangement of Aminomethylsilanes to Methylaminosilanes

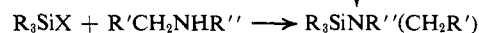
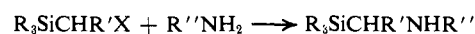
Sir:

Considerable attention has been focused in recent years on the subject of 1,2-anionic rearrangements of organosilicon compounds.¹



Known examples of this type of reaction are the silylcarbinol-alkoxysilane rearrangement² and its reverse³ (X = C, Y = O), the benzylthiotrimethylsilane-

curred in high yield at room temperature or at 100°, depending on the amine. The reactions could be conveniently carried out in sealed nmr tubes and the relative rates were determined by spectroscopic examination of the solution. The rearrangement products were identified by gas chromatographic and spectral comparison with authentic samples prepared by alternative methods.



Our preliminary rate studies indicate that the reaction obeys pseudo-first order kinetics and the following observations are believed to be significant: (a) aminobenzylsilanes (R' = Ph) rearrange more rapidly than aminomethylsilanes (R' = H); (b) *N*-methyl compounds rearrange more rapidly than *N*-benzyl-, *N*-isopropyl-, or *N*-cyclohexylamines; (c) silylmethyl-anilines do not appear to rearrange under any conditions investigated. These facts are in accord with a rearrangement mechanism, analogous to that proposed for the silylcarbinol-alkoxysilane rearrangement, in which an initially generated nitrogen anion undergoes a 1,2-migration of silicon from carbon to nitrogen. The resultant carbanion can in turn abstract a proton

Table I. Rearrangements of Secondary Aminomethylsilanes Catalyzed by *n*-Butyllithium

Aminomethylsilane	Equiv of <i>n</i> -BuLi	Reaction conditions ^a temp, °C	time, hr	Silylamines ^b
Me ₃ SiCH ₂ NHCH ₂ Ph	0.10	100	40	Me ₃ SiNMeCH ₂ Ph (A)
Me ₃ SiCH ₂ NHC ₆ H ₁₁	0.10	100	0.5	Me ₃ SiNMeC ₆ H ₁₁ (A)
Ph ₃ SiCH ₂ NHCH ₂ Ph	0.17	25	37	Ph ₃ SiNMeCH ₂ Ph (B)
Me ₃ SiCHPhNHMe	0.10	25	1	Me ₃ SiNMeCH ₂ Ph
Me ₃ SiCHPhNH- <i>i</i> -Pr	0.10	25	36.5	Me ₃ SiN(CH ₂ Ph)- <i>i</i> -Pr (B)
Me ₃ SiCHPhNHC ₆ H ₁₁	0.20	25	60	Me ₃ SiN(CH ₂ Ph)C ₆ H ₁₁ (B)
Me ₃ SiCHPhNHC ₆ H ₁₁	0.20	100	0.25	Me ₃ SiN(CH ₂ Ph)C ₆ H ₁₁ (B)
Me ₃ SiCHPhNHCH ₂ Ph	0.10	25	24	Me ₃ SiN(CH ₂ Ph) ₂ (B)
Me ₃ SiCH ₂ NHPh	0.10	100	40	No reaction
Me ₃ SiCHPhNHPh	0.10	100	40	No reaction

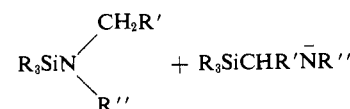
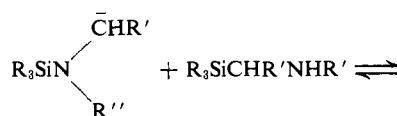
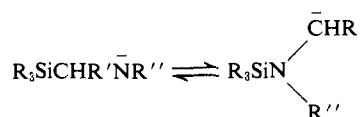
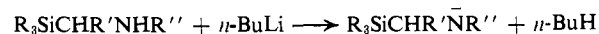
^a Rearrangements carried out in benzene solution in nmr tubes sealed under nitrogen. ^b Method of alternative synthesis: A, R₃SiCl + R'R''NH + Et₃N; B, R'R''NLi + R₃SiCl.

α-trimethylsilylbenzyl mercaptan rearrangement⁴ (X = S, Y = C), the silylhydrazine rearrangement⁵ (X = Y = N), and the rearrangement of 1,1-bis(trimethylsilyl)-1,2-diphenylethane⁶ (X = Y = C).

We wish to report a new example of this type of reaction, the base-catalyzed rearrangement of secondary aminomethylsilanes to the isomeric aminosilanes (X = C, Y = N).

When benzene solutions of a variety of aminomethyl- and aminobenzylsilanes (Table I), prepared by the method of Speier,⁷ were treated with a small amount of *n*-butyllithium (0.1–0.2 equiv) the rearrangement oc-

curred from the parent amine to give the product and regenerate the nitrogen anion.



Thermodynamic calculations using available bond energies suggest that the overall reaction will vary in

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exothermicity from approximately 2 to 20 kcal/mol depending on the nature of R' and R''.

The proposed mechanism accounts for the more rapid rearrangement of the benzylaminosilanes (R' = Ph) where stabilization of the carbanion relative to the nitrogen anion would occur and the lack of rearrangement of the anilines (R'' = Ph) where stabilization of the nitrogen anion relative to the carbanion should exist. Attempts to investigate the reverse reaction by metalation of the benzyl carbon of compounds such as *N*-trimethylsilyldibenzylamine using excess *tert*-butyllithium or the *n*-butyllithium-tetramethylethylenediamine complex have now been made successfully. More detailed studies of the scope and mechanism of this rearrangement are in progress.

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A. G. Brook,* J. M. Duff[§]

Lash Miller Chemical Laboratories, The University of Toronto
Toronto, Ontario, Canada

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Estimation of Solvolysis Rates of Cyclic Secondary Substrates

Sir:

A major difficulty in the controversy surrounding the importance of anchimeric assistance in the solvolysis of secondary alkyl derivatives¹⁻⁵ has been the inability to predict solvolysis rates of cyclic substrates.⁶ One method of performing such predictions is by use of a form of the Taft σ^* linear free energy relationship, eq 1.⁷⁻¹¹ For example, solvolysis rates of acyclic deriva-

$$\log k/k_0 = \sigma^* \rho^* \quad (1)$$

tives are correlated by the σ^* treatment, and positive deviation from this correlation has been taken as evidence for anchimeric assistance.^{8,9,11} Unfortunately, σ^* constants are not available for cyclic systems and, in certain significant cases, cannot be determined by the usual methods.^{7,12}

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We have developed a method for prediction of solvolysis rates of secondary cyclic systems (1) which is based on solvolysis rates of the corresponding methyl-substituted tertiary derivatives (2). A linear σ^* plot



is observed for the solvolysis of acyclic tertiary chlorides in 80% aqueous ethanol ($\rho^* = -3.29$)¹¹ and of the *p*-nitrobenzoates in 60% aqueous acetone ($\rho^* = -2.2$).¹³ By placing the rates of cyclic tertiary derivatives, 2, on these plots, σ^* values (designated σ_t^*) can be determined. These σ_t^* values will accurately reflect inductive, hyperconjugative, and steric effects for solvolysis of a secondary cyclic alkyl system if there are no major steric differences between the secondary derivatives and the tertiary models. Substitution of a methyl group onto cyclic (e.g., cyclopentyl) and polycyclic (e.g., 2-norbornyl and 2-adamantyl) systems has been shown to contribute little to ground-state steric strain.^{14,15} Exceptions are the medium rings and certain polyalkylated norbornyl derivatives; use of the σ_t^* method for treatment of these complex substrates is deferred.

Use of σ_t^* and eq 1 should yield calculated rates for secondary substrates accurate within a factor of 10, with this variation due to temperature and solvent extrapolations and uncertainties in σ^* plots (a factor of 2), and to minor steric variations (a factor of 5). In fact, the average deviation for model substrates is only a factor of 2.

Reaction constants (ρ^*) are known for the acetolysis ($\rho^* = -2.6$)^{10,16} and aqueous ethanolysis ($\rho^* = -1.92$ in 80% ethanol)¹⁷ of acyclic derivatives. These reactions have been clearly shown^{9,16,18-20} to involve nucleophilic solvent assistance (a k_s process)¹⁸ equivalent to a rate factor of 10^2 - 10^4 . Thus, use of these ρ^* values yields calculated rates which include assistance of 10^2 - 10^4 .

Comparison of predicted and observed solvolysis rates for several model k_s substrates^{18,20,21} (1-6) shows

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