

Table I. Arrhenius Parameters and Tunnel Corrections for the Reaction of 3-Methyl-2-butyl *p*-Nitrobenzenesulfonate with Alkoxides in the Corresponding Alcohols

quantity ^a	alkoxide	
	EtONa	<i>t</i> -BuOK
(<i>A</i> _{aH} / <i>A</i> _{aD}) _{1-ene}	0.247 ± 0.037	0.174 ± 0.039
(<i>A</i> _{aH} / <i>A</i> _{aD}) _{2-ene}	1.053 ± 0.186	0.641 ± 0.191
(<i>E</i> _{aD} - <i>E</i> _{aH}) _{1-ene} ^c	1.580 ± 0.102	1.928 ± 0.162
(<i>E</i> _{aD} - <i>E</i> _{aH}) _{2-ene} ^c	0.479 ± 0.107	0.801 ± 0.187
(<i>k</i> _H / <i>k</i> _D) _{obsd} , 1-ene ^b	3.39	4.30
(<i>k</i> _H / <i>k</i> _D) _{obsd} , 2-ene ^b	2.33	2.43
(<i>Q</i> _{tH} / <i>Q</i> _{tD}) _{1-ene}	2.00	2.44
(<i>Q</i> _{tH} / <i>Q</i> _{tD}) _{2-ene}	1.00	1.42
(<i>k</i> _H / <i>k</i> _D) _s , 1-ene	1.69	1.77
(<i>k</i> _H / <i>k</i> _D) _s , 2-ene	2.33	1.72
<i>Q</i> _{tH} (1-ene)	3.37	4.48
<i>Q</i> _{tH} (2-ene)	1.00	1.91
(<i>k</i> _{2-ene} / <i>k</i> _{1-ene}) _{obsd} ^b	4.6	0.48
(<i>k</i> _{2-ene} / <i>k</i> _{1-ene}) _s	15.5	1.13

^a Temperature-dependent quantities are for 30 °C in all cases.

^b Calculated from the Arrhenius parameters rather than directly observed, so as to smooth random variations prior to the computer fits.

^c kcal mol⁻¹.

*k*_H/*k*_D and *k*_{2-ene}/*k*_{1-ene}—those values that would be observed in the absence of tunneling—can be calculated, since

$$(k_H/k_D)_{\text{obsd}} = (Q_{tH}/Q_{tD})(k_H/k_D)_s$$

and

$$(k_{2-ene}/k_{1-ene})_{\text{obsd}} = [Q_{tH}(2-ene)/Q_{tH}(1-ene)](k_{2-ene}/k_{1-ene})_s$$

The Arrhenius parameters and the various quantities derived from them are collected in Table I.

It is obvious, both qualitatively from the Arrhenius parameters and quantitatively from the dissection into tunnel corrections and semiclassical values, that tunneling does significantly affect the ratio of Saytzev to Hofmann product in this typical E2 reaction. Discussions of orientation⁸ customarily consider the influence of inductive, hyperconjugative, and steric effects on the relative free energies of the respective transition states. Such thermodynamic comparisons necessarily ignore the strictly kinetic phenomenon of tunneling; so we should direct our attention to (*k*_{2-ene}/*k*_{1-ene})_s, not (*k*_{2-ene}/*k*_{1-ene})_{obsd}. When we do so with the present data, a fairly strong observed preference for the Saytzev product (2-ene) with ethoxide-ethanol becomes much stronger, and the modest observed preference for the Hofmann product (1-ene) with *tert*-butoxide-*tert*-butyl alcohol disappears. Substantial differences between orientation in the two media remain, of course, but revisions in our evaluation of the factors determining orientation are certainly in order. We have experiments in progress to delineate further the role of tunneling in orientation in E2 reactions. Until more data are available, it seems pointless to discuss just what changes in theories of orientation may be necessary.

It is interesting to speculate briefly on why tunneling should be more important in formation of the Hofmann than the Saytzev product. At first sight, it goes against the idea that greater steric congestion in the transition state should facilitate tunneling.³ We suggest that the difference in steric effects between the reactions forming 1-ene and 2-ene may not be great enough to bring this factor into play. It is likely, however, that the transition state leading to the Saytzev product has more double-bond character than that leading to the Hofmann product, which would result in more heavy-atom motion in the reaction coordinate.^{6,9} The movement apart of the two β-methyl groups as the β carbon goes from sp³ to sp² should add further to this heavy-atom motion. Both types of heavy-

atom motion should tend to decrease the contribution of tunneling.

The semiclassical isotope effects show a distinctly different pattern from the observed ones. The larger observed isotope effects on 1-ene than 2-ene formation result entirely from tunneling, as does the larger isotope effect for 1-ene formation with *tert*-butoxide than with ethoxide. The fact that (*k*_H/*k*_D)_s on 2-ene formation is no smaller than that on 1-ene formation (indeed, with ethoxide-ethanol it appears somewhat larger) argues against the suggestion that Saytzev products are formed via more E2C-like transition states than Hofmann products.^{10,11} The E2C transition state is postulated to have a base-hydrogen-carbon angle substantially less than the 180° of the E2H transition state,¹⁰ and reactions with nonlinear transition states should have smaller (*k*_H/*k*_D)_s values than those with linear transition states.¹²

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- (11) Reference 10 reports a (*k*_H/*k*_D)_{1-ene} of 6.3 at 50 °C for the reaction of 3-methyl-2-butyl tosylate with ethoxide in ethanol, where *k*_H and *k*_D were calculated from the overall rates of elimination + substitution, fractions of elimination, and fractions of 1-ene for the respective isotopic species. Our (*k*_H/*k*_D)_{1-ene} at 50 °C is only 2.9, and it seems unlikely that the change of leaving group would affect *k*_H/*k*_D so much. Any secondary isotope effect on elimination into the undeuterated branch of **3** would make our *k*_H/*k*_D lower than the strictly intermolecular effect of ref 10, but so large a secondary effect seems even more unlikely. While we cannot explain the discrepancy, we believe our *k*_H/*k*_D values are more reliable because they are based on 1-ene:2-ene ratios only, rather than the complex dissection of observed rates of ref 10. In support of this view, our data on 1-ene:2-ene ratios agree fairly well with those reported in ref 10.
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²⁹Si NMR Studies of Relatively Stable Silaethylenes

Sir:

Recently the conversion of pivaloyltris(trimethylsilyl)silane (I) into the isomeric silaethylene II, which exists in solution in equilibrium with its dimer III, was described.¹ Of particular

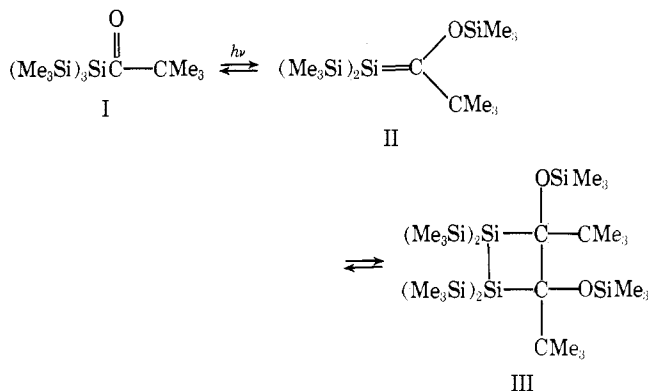


Table I. ^{29}Si NMR Absorptions for Acylsilanes and Derivatives

compd	conditions ^a	Si ^a	Si ^b	Si ^{c,d}	Si ^e	Si ^f	Si ^{g,h}	Si ⁱ	Si ^j
$(\text{Me}_3\text{Si})_3\text{SiCPh}$	2 M CDCl_3 + Me_4Si C_6D_6 + Me_4Si	-11.33 -11.35	-71.22 -72.25						
$(\text{Me}_3\text{Si})_3\text{SiCPh}$ + dimer III ($\text{R}' = \text{Ph}$), 1:1	0.5 M each, CDCl_3	-11.35	-71.05				-12.02, -13.19	-40.46	8.95 ^b
III ($\text{R}' = \text{Ph}$)	0.5 M CDCl_3 + Me_4Si						-12.02, -13.21	-40.38	8.94
$(\text{Me}_3\text{Si})_3\text{SiCPh}$	3 M C_6D_6 , photolyzed, NMR in CDCl_3						-12.02, -13.21	-40.39	8.98 ^b
$(\text{Me}_3\text{Si})_3\text{SiC}$ -	2 M C_6D_6	-11.39	-72.20						
$(\text{Me}_3\text{Si})_3\text{SiC}$ -	2 M C_6D_6 , photolyzed, added 3 vol. of Et_2O for NMR						-12.01, -13.36	-40.90	8.29 ^c
$(\text{Me}_3\text{Si})_3\text{SiCOCMe}_3$	2 M CDCl_3 + Me_4Si	-11.52	-76.62						
$(\text{Me}_3\text{Si})_3\text{SiCOCMe}_3$	2 M C_6D_6 + Me_4Si	-11.42	-77.66						
$(\text{Me}_3\text{Si})_3\text{SiCOCMe}_3$	2 M C_6D_6 , photolyzed	-11.49	-77.90	-12.18, -12.64	41.44	13.34	-9.50, -10.88	-43.78	-0.05
III ($\text{R}' = \text{CMe}_3$)	1 M C_6D_6	-11.46	-77.73	-12.15, -12.65	41.51	13.45	-9.46, -10.80	-43.70	+0.01
$(\text{Me}_3\text{Si})_3\text{SiCOCPh}_3$	C_6D_6	-10.73	-66.53						
$(\text{Me}_3\text{Si})_3\text{SiCOCEt}_3$	2 M C_6D_6 + Me_4Si	-11.32	-78.16						
$(\text{Me}_3\text{Si})_3\text{SiCOCEt}_3$	2.5 M C_6D_6 , photolyzed, then Me_4Si	-11.33	-78.18	-11.79, -12.19	54.26	12.74			^e
$(\text{Me}_3\text{Si})_3\text{SiCO}$ - adamantyl	1 M C_6D_6	-11.42	-76.90						
$(\text{Me}_3\text{Si})_3\text{SiCO}$ - adamantyl	2 M C_6D_6 , photolyzed	-11.49	-78.68	-12.31, -12.62	41.80	13.39			^f
$(\text{PhMe}_2\text{Si})_3\text{-}$ SiCOCMe_3	1 M C_6D_6	-14.16	-75.82						

^a Approximate concentrations of compound in solvent listed, with internal Me_4Si if mentioned. NMR run at ambient temperature, usually 32°C , for 16–24 h with most mixtures and for 4–6 h for pure compounds. Photolyses run for 24 h at 11°C prior to NMR investigation. ^b Minor unknown absorption at 23.16 ± 0.03 . ^c Major dimer. ^d Minor dimer. ^e Additional small absorptions at -9.39 , -9.70 . ^f Minor unknown absorptions at -8.87 , -9.70 , and -10.04 ppm.

interest was the remarkable room-temperature stability of the silaethylene which could be observed by NMR over a 2-week period as it slowly reverted to I and, also, the fact that III appeared to be the head-to-head 1,2-disilacyclobutane dimer, in contrast to the commonly observed 1,3-disilacyclobutane dimers formed from more simply substituted silaethylenes.²

The crystal structure of III has now been determined by X-ray analysis, confirming the 1,2-disilacyclobutane structure and showing that a trans relationship exists between the two trimethylsilyloxy groups about the four-membered ring (see Figure 1). The ring is almost planar with no atom deviating >0.10 Å from its least-squares plane.

While the Me–Si bonds are of normal length (average 1.91 Å), the ring Si–C bonds (average 2.00 Å) are rather longer than usual, as is the ring Si–Si bond at 2.37 Å and the Me_3Si –Si bonds (average 2.43 Å). These values may be compared with those found for $(\text{Me}_3\text{Si})_3\text{SiRe}(\text{CO})_5$,³ where the Me_3Si –Si bonds were 2.37 Å, and for the unusual bis-(*exo*-methylene)-1,2-disilacyclobutane recently described by Ishikawa et al.,⁴ where the ring Si–Si bond was 2.34 Å, the ring Si–C bonds averaged 1.93 Å, and the C–C ring bond was 1.43

Å. In our compound, the ring C–C bond (1.66 Å) is remarkably long, which is consistent with considerable stretching caused by steric repulsion from adjacent bulky groups and also with possible homolysis of the bond to a 1,4 diradical, as suggested by ESR studies.^{1,5}

We have found ^{29}Si NMR to be a very useful tool for studying the silaethylenes II and related compounds. As shown in Table I, all acylsilanes $(\text{Me}_3\text{Si}^a)_3\text{Si}^b\text{COR}'$ show two ^{29}Si absorptions, in the region of about -11 ppm for the trimethylsilyl groups Si^a and at about -71 to -78 ppm for the central silicon Si^b .^{6,7} The known stable dimer III ($\text{R}' = \text{Ph}$), studied separately, shows four absorptions, two for the trimethylsilyl groups at -12 and -13 ppm, one for the trimethylsilyloxy group at $+8.9$ ppm, and one for the ring silicon at about -40 ppm. Other dimers with different R' can be expected to have absorptions very close to these positions, as was found for III ($\text{R}' = 3,5$ -dimethylphenyl) where a mixture of two isomers was formed on photolysis.

We have found it possible to study the complex system $\text{I} \rightleftharpoons \text{II} \rightleftharpoons \text{III}$ for several compounds. Figure 2 shows the ^{29}Si spectrum obtained from the solution obtained from photolysis

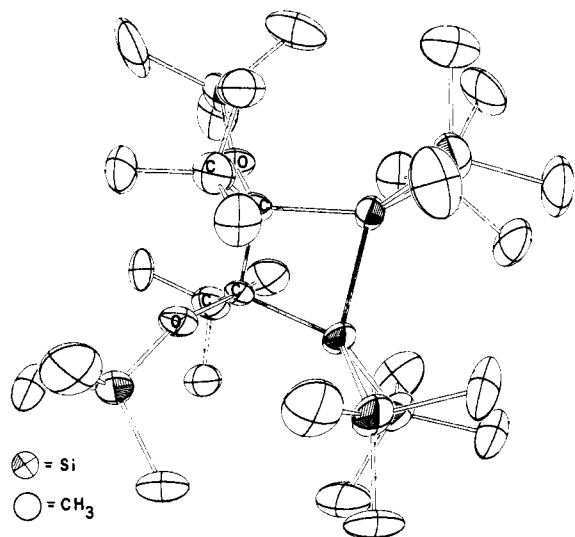


Figure 1. ORTEP plot of nonhydrogen atoms of silaethylene dimer III ($R' = t\text{-Bu}$) showing 50% probability ellipsoids.

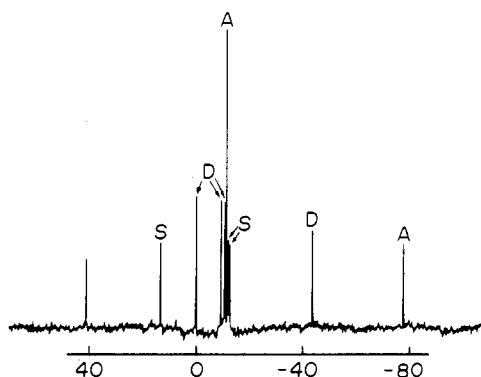


Figure 2. ^{29}Si spectrum of solution from photolysis of $(\text{Me}_3\text{Si})_3\text{SiCOCMe}_3$ in C_6D_6 with signals attributable to acylsilane I (A), silaethylene II (S), and its dimer III (D) in parts per million relative to Me_4Si .

of the acylsilane I ($R' = t\text{-Bu}$), a spectrum virtually identical (except for relative intensities) with that observed merely by dissolving the pure solid dimer III ($R' = t\text{-Bu}$) in C_6D_6 at room temperature immediately prior to taking the NMR spectrum. The spectrum is characterized by three sets of signals, the bands at -11.49 and -77.90 being due to the acylsilane and those at -0.05 , -9.50 , -10.88 , and -43.78 being due to dimer III. The remaining four bands of approximately equal intensity can be ascribed to the monomer II, the bands at -12.18 and -12.64 being due to Me_3Si groups, that at 13.34 to the trimethylsiloxy group, and the band at the very unusual low-field position at 41.44 ppm being consistent with an unusually hybridized silicon atom as would be found in a silaethylene.

This assignment, together with the previously observed ^{13}C signal at δ 112.7 ppm for the sp^2 -hybridized carbon atom, fully characterizes the silicon-carbon double bond, a species that we regard as not significantly polarized (see reference 1), consistent with its unusual head-to-head dimerization, probably by radical coupling at silicon.

In contrast to the pivaloylsilane, where the photolysis system shows the presence of acylsilane, monomer and dimer, replacement of R' in the acylsilane by the bulkier groups CtEt_3 or adamantyl gives photolysis solutions which show evidence for acylsilane and silaethylene only, but no dimer. This result is in accord with our anticipation that increasing the bulk of the groups attached to either the sp^2 -hybridized carbon or silicon of the silaethylene would stabilize the monomer relative to the dimer because of increased steric strain in the latter. However, the increased bulk about carbon appears to also

destabilize the silaethylene relative to the acylsilane. A photostationary state apparently develops between the species so that extended photolysis fails to reduce the amount of acylsilane, and, when the light is removed, the silaethylene returns to acylsilane more rapidly than was observed with the pivaloylsilane.

It is clear that these complex systems can be conveniently studied by ^{29}Si NMR, and the present data, taken with that reported earlier, establish unequivocally the presence of remarkably stable silaethylenes in these systems. Stabilization of the silaethylenes by increasing the bulk of the groups attached to carbon is not a straightforward matter. Further studies are in progress.

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- (5) The dimer III crystallizes in monoclinic system, space group $P2_1/c$, with a unit cell of dimensions $a = 12.21$ (6), $b = 22.31$ (4), $c = 18.18$ (7) Å; $\beta = 120.3$ (7) $^\circ$; and $Z = 4$. The crystal structure is still being refined ($R = 0.082$), not all the hydrogen atoms having yet been found. No significant changes in interatomic distances are expected. Full details will be published elsewhere by S. C. Nyburg and J.-S. Lee.
- (6) All spectral data are relative to Me_4Si . Spectra were measured at 15.9 MHz, using a pulse flip angle of 45° , a pulse repetition time of 25 s, and gated decoupling to suppress nuclear Overhauser effects. Even with these precautions, the relative proportions of different species present could not always be reliably determined from the relative intensities of the ^{29}Si signals since artificial mixtures of compounds showed proportions in error by factors ranging from 1.5 to >3.3 , depending upon the silicon signals being compared. In particular the central ^{29}Si signal of acylsilane I is often of lower than expected intensity, suggesting an extremely long spin-lattice relaxation time for this silicon.
- (7) Satisfactory elemental analysis and ^1H NMR, IR, and mass spectral data were obtained for all new compounds.

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Spherands—Ligands Whose Binding of Cations Relieves Enforced Electron-Electron Repulsions¹

Sir:

The crowns,² cryptands,³ and natural ionophores⁴ owe their metal-ion binding properties to varying degrees of organization (prior to complexation) of functional groups containing oxygen and nitrogen. In these hosts, the unshared electron pairs of their heteroatoms become focussed on cations during complexation by conformational reorganizations of their supporting chains. The X-ray structures of these hosts do not show the presence of the holes, which in their complexes are filled with metal ions. Rather, potential cavities in hosts are filled by a folding inward of their parts which turn outward when "displaced" by guests.⁵ Thus the guest conformationally organizes some of the binding