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# Reactivity and Selectivity in the Cyclization of Sila-5-hexen-1-yl Carbon-Centered Radicals[1]

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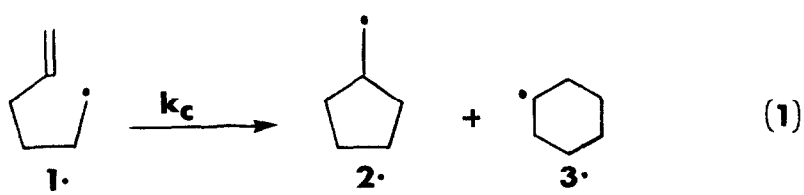
## Summary

A trio of sila-5-hexen-1-yl radicals has been prepared from the corresponding halides by reaction with tri-*n*-butyltin hydride (deuteride). The radicals possessing a dimethylsilyl function α or β to the carbon radical center demonstrated marked reduction in total (but especially exo-trig) cyclization compared to the all-carbon system. The γ-silyl radical behaved, contrariwise, quite comparably to the all-carbon system. The difference in cyclization found in the α-silyl radical was demonstrated to result from both a pronounced decrease in cyclization rate via the expected exo-trig mode and from a significantly enhanced rate of hydrogen abstraction from TBTH. Both the α- and γ-silyl radicals cyclized via the endo-trig mode at rates close to that of the parent 5-hexen-1-yl radical itself. The cyclizations studied were demonstrated to be irreversible. The kinetic control thus shown by the preferred formation of endo cyclized product from the α- and β-silyl radicals is highly unusual and represents the first report of carbon-centered 5-hexen-1-yl type radicals violating the Baldwin-Beckwith rule (exo-trig cyclization preferred by 5-hexen-1-yl radicals). Rationalization of the cyclization behavior of the α- and γ-silyl radicals involves both steric and electronic factors. The behavior of the most unusual case, the β-silyl radical, which has the lowest cyclization propensity and no exo mode product, remains largely unexplained because its hydrogen abstraction rate from TBTH is unavailable as yet. Some speculative considerations involving the preferred radical conformation in this system and its relation to cyclization are given.

## Introduction

By now it is generally known that the 5-hexen-1-yl radical (1•) cyclizes readily (eqn. 1).[2]



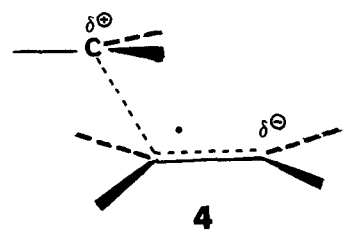

(1)

Equally familiar is the high contrathermodynamic regioselectivity of this cyclization; formation of less stable $\underset{\sim}{2}\bullet$ grossly exceeds that of more stable $\underset{\sim}{3}\bullet$. The cyclization has been studied in great detail, primarily in recent years by Beckwith and co-workers.[3] Their cyclization data, when coupled with kinetic data from Ingold's laboratory[4], have led to the following Arrhenius expression for the cyclization rate constant $k_c$ (eqn. 2),

$$\log k_c = (10.42 \pm 0.32)-(6.85 \pm 0.42)/\theta \qquad (2)$$

where $\theta$ = 2.303 RT. This cyclization therefore has become somewhat of a standard, against which other radical processes are compared, particularly with respect to rate.[5] Being thusly some type of "standard", equation 1 has been termed a "radical clock". Indeed it has become the Greenwich Meridian Time of radical chemistry![6]

The cyclization has been reviewed thoroughly[2], thankfully, because the number of "5-hexen-1-yl type" cyclizations reported has increased dramatically in recent years. Studies on various analogues of $\underset{\sim}{1}\bullet$ have demonstrated that no simple explanation exists for the contrathermodynamic stereoselectivity exhibited in these cyclizations. The presently preferred view is that first advanced by Beckwith[7] and later supported by Baldwin.[8] This view, expressed as the "Baldwin-Beckwith rules" uses the terms "exo" and "endo" for radical addition to the internal and terminal atoms of the double (or triple) bond, respectively. The additional descriptors "trig" or "dig" apply to the trigonal or digonal nature of the acceptor atom. The preferred exo-trig formation of $\underset{\sim}{2}\bullet$ over the endo-trig formation of $\underset{\sim}{3}\bullet$ has been explained as shown below in $\underset{\sim}{4}$.



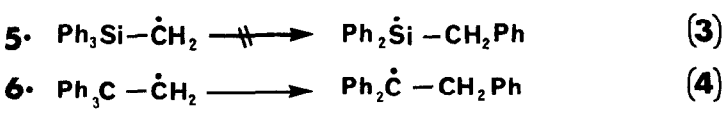

**4**

In $\underset{\sim}{4}$, the donor nature of attacking carbon-centered radicals and the acceptor nature of the double bond are reflected in the dipolar nature of the structure. Note that the three carbon atoms form a triangular array perpendicular to the $\pi$-nodal plane. Models buttressed with various calculations[9] have indicated that exo cyclization is geometrically easier than endo in this regard. Because oxy

and aza radicals behave similarly[2] - even though certainly not donor radicals by nature - this steric ease of formation must be more significant in these examples than the dipolar (electronic) character of 4. The factors involved in the cyclization are subtle and their interaction fragile.[10] Although exo cyclization by carbon-centered radicals is the rule, substitution that encumbers the double bond and/or reversibility in the addition clearly changes the regioselectivity of the process.[2] Moreover, the applicability of the Baldwin-Beckwith rules to such cyclizations where the radical center is not a first row element is far less secure. Two recent studies have demonstrated endo cyclization for silicon-centered radicals.[11] Sulfur radicals also cyclize with endo selectivity[12] (though here reversibility may complicate the picture), whereas phosphorus radicals still prefer the exo mode.[13] Radical centers other than carbon, of course, introduce potential hybridizational problems (planar vs. pyramidal), along with changed bond lengths, to an already complex situation. Considering the precarious balance of all these effects, predictions about regioselectivity can understandably be risky.

Finally, the cyclization has now become part of synthetic methodology.[14] This switch from its study by mechanicians to its use by creative methodologists has contributed significantly to the burst of interest in the cyclization. It is therefore indeed apt to include this cyclization with its attendant selectivity and synthetic application in a Symposium-in-Print devoted to such a topic.

Interest in this cyclization by this Laboratory arose from an on-going interest in the relationship between the respective chemistry of all carbon radicals and their silicon-containing relatives. Some time ago the curious observation that radical 5 would not rearrange (eqn. 3) in contrast to the easy rearrangement of 6• (eqn. 4)[16],



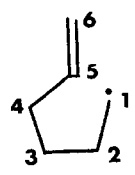

(3)

(4)

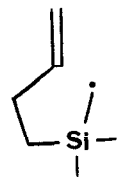
led to a more systematic study of such radicals.[17] A result of that study showed that α-halosilanes are much more easily reduced by tri-n-butyltin hydride (TBTH) than the corresponding haloalkanes. Now, among the most studied of haloalkane-TBTH reactions is that exemplified by eqn. 1. Consequently it was of interest to determine the effect of a silicon function situated at various sites on the progress of this reaction.

## Results and Discussion

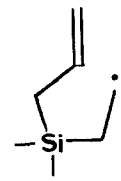
Inspection of the 5-hexen-1-yl radical $\underset{\sim}{1}\bullet$ reveals three potential sites for silicon substitution. These are shown as α-$\underset{\sim}{1}\bullet$, β-$\underset{\sim}{1}\bullet$, and γ-$\underset{\sim}{1}\bullet$.



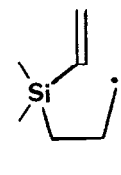

**1•**




**α–1•**

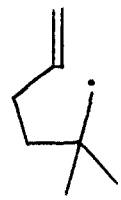



**β–1•**




**γ–1•**

The remaining sites would involve either a silicon-centered radical (position 1) - not a goal of this research[18] - or a silene (positions 5 or 6) - an unstable type of substance[19] that would render synthesis of precursors too difficult. The silicon substituent chosen was dimethyl silyl, $(CH_3)_2Si<$, largely because the precursor problem would be minimized. It should be recognized at the outset that at least three significant changes result when $\underset{\sim}{1}\bullet$ is conceptually converted to its silicon-containing analogues. First, the longer carbon-silicon bond (1.91 Å) now present could influence the cyclization in some way. Second, non-bonded interactions involving an axial methyl group could affect the six-membered ring transition state for endo cyclization. Third, the cyclization would be definitely affected by any change in the chain transfer reaction (hydrogen atom abstraction) of these radicals with TBTH. Of these three potential sources for disparate behavior, the third could be managed to a degree by varying the concentration of TBTH. The others are intrinsic to the structures and offer no control, although the conformational problem involving the axial methyl group could perhaps be better analyzed by comparison of the silicon species with $\underset{\sim}{7}\bullet$ instead of $\underset{\sim}{1}\bullet$, particularly as some cyclization data is available for $\underset{\sim}{7}\bullet$.[20]



**7·**

Because the popular reactants for TBTH are halides,[21,22] α-1-Cℓ, β-1-Cℓ, and γ-1-Br were needed. One may note that in usual carbon systems, bromides are commonly employed with TBTH because most chlorides are reduced too slowly at moderate temperatures. As previously mentioned, however, α-chlorosilanes are easily reduced by TBTH, even at 25°C.[17] Moreover, though less reactive than the α cases, even β-chlorosilanes are reduced at a practical rate. Hence the choice of chloride precursors for α-1· and β-1·. The enhanced reactivity is not apparent for γ-chlorosilanes, so here a bromide precursor was selected. Chloride α-1-Cℓ was prepared as described by Connolly and Fryer.[23] The other halides were unreported heretofore. In Scheme 1 are shown the synthetic paths used to prepare all three.

**Scheme 1**

$$CH_2{=}CHCH_2CH_2Br \xrightarrow{a,b} CH_2{=}CHCH_2CH_2{-}SiMe_2CH_2Cl$$

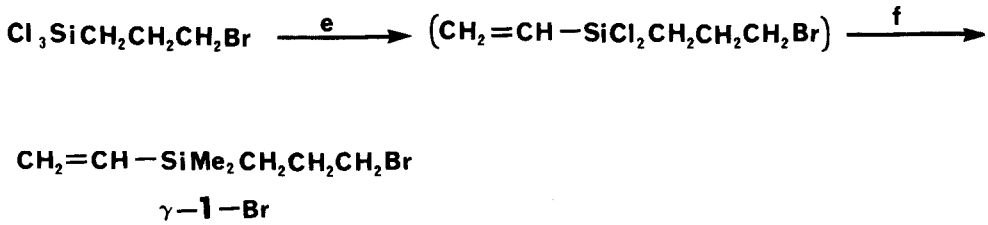
α−1−Cl

$$CH_2{=}CHCH_2MgCl \xrightarrow{b} CH_2{=}CHCH_2{-}SiMe_2CH_2Cl \xrightarrow{c}$$

**8**

$$CH_2{=}CHCH_2{-}SiMe_2CH_2CH_2OH \xrightarrow{d} CH_2{=}CHCH_2{-}SiMe_2CH_2CH_2Cl$$

**9** β−1−Cl

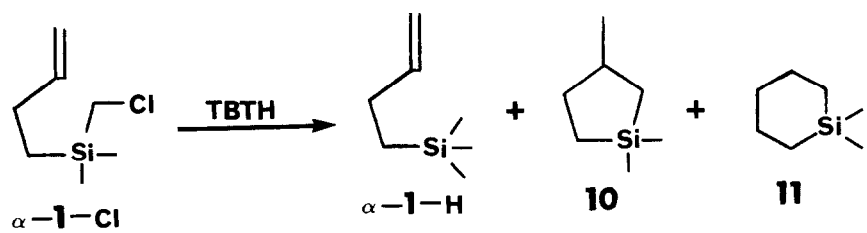


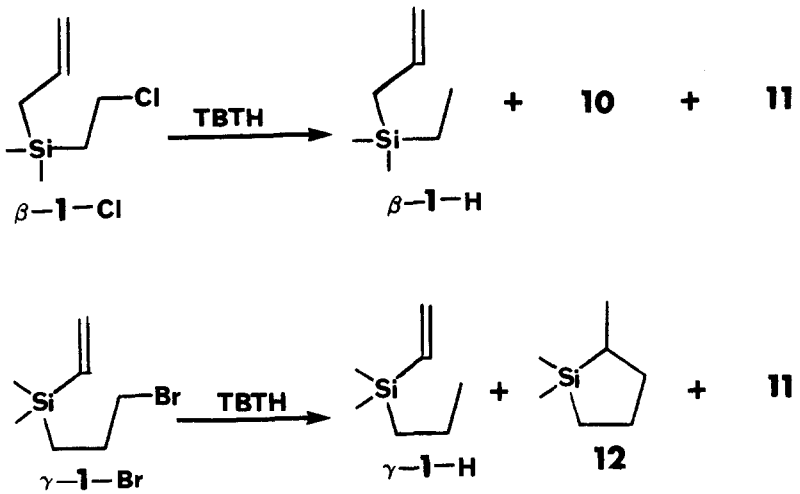

a: Mg, $Et_2O$
b: Cl−$SiMe_2CH_2Cl$, Δ
c: HCHO
d: $SOCl_2$, TMP
e: $CH_2$=CHMgBr, THF,
f: MeMgBr, $Et_2O$, Δ

The reactions used in Scheme 1 are straightforward and the details are reserved for the Experimental Section. The halides and their isolated precursors were oils and they were characterized in standard fashion by analysis and consonant spectra.

The reduction of these halides with TBTH led to unsaturated and cyclic silanes, as shown in Scheme 2.

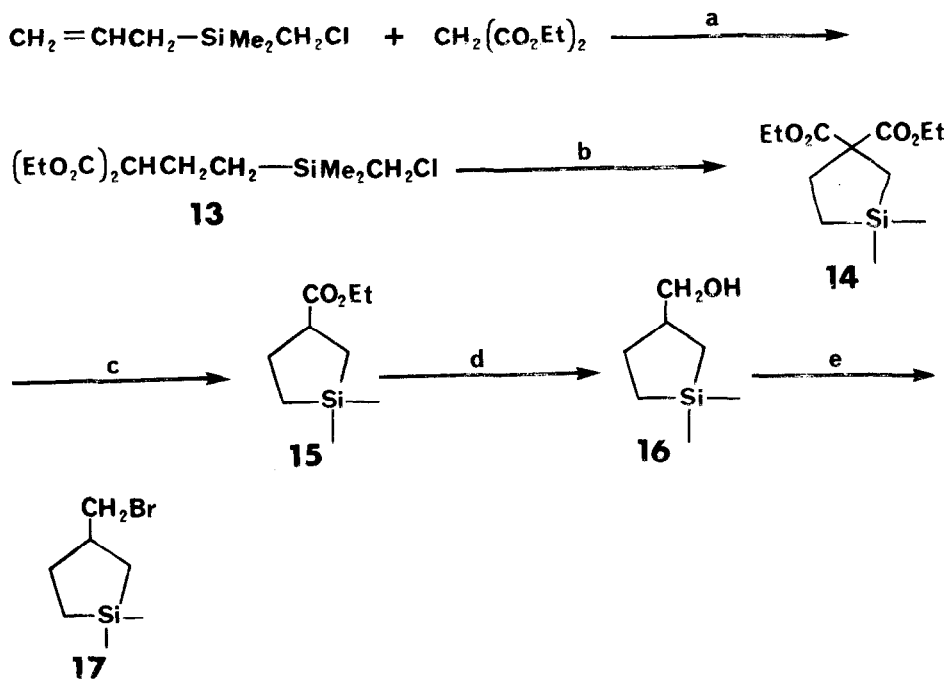
## Scheme 2






All of these silanes have been reported and they were synthesized by the literature methods. The combined yields of 10 and 11 (for α-1-Cℓ and β-1-Cℓ) and of 11 and 12 (for γ-1-Cℓ) represent the degree of cyclization for these systems when compared to the yields of cycloalkanes obtained from 1• under comparable reaction conditions. The ratio of 10 to 11 or 12 to 11 similarly reflects the regioselectivity of these cyclizations. It was observed that both the degree of cyclization and the regioselectivity shown by the α and β cases differed significantly from the all-carbon analogue, whereas the γ system closely resembled the all-carbon model. It would appear that the results obtained for the α and β systems represent the first deviation by carbon-centered radicals from the Baldwin-Beckwith rules, provided that reversibility of the cyclization is absent. Clearly the other known[2] cause for deviant cyclization, addition to a sterically crowded double bond, is not present in the systems used here. But is the cyclization irreversible? Is kinetic control involved? To test this point, bromide 17 was prepared as shown in Scheme 3.

## Scheme 3




a: *t*-BuO—O*t*-Bu, Δ

b: NaOEt, EtOH, Δ

c: LiCl, $Me_2SO$, Δ

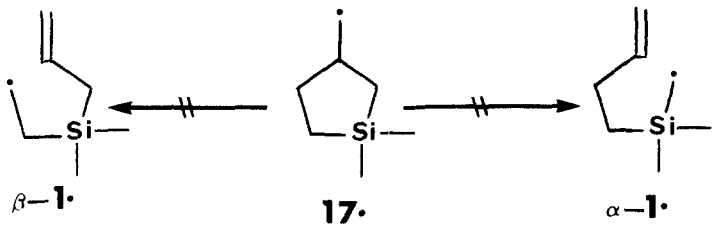
d: $LiAlH_4$, $Et_2O$

e: TsCl, Pyr / LiBr, $Me_2CO$, Δ

Rarely performed but quite useful synthetically[24], the free radical addition of malonic ester to terminal alkenes, in this case (chloromethyl)vinyldimethylsilane, readily afforded the adduct 13. The subsequent steps in Scheme 3 followed well-known procedures. Again standard characterization data was obtained for

isolated compounds in the sequence.

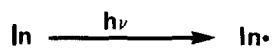
Reduction of bromide 17 with TBTH formed only cyclosilane 10. No evidence was found for ring opening of radical 17• to α-1• or β-1• (eqn. 5), even at the high 17: TBTH concentration ratio used, where radical lifetimes would be longer.




(5)

It may be concluded therefore that the reductions of the 1- halides with TBTH are kinetically controlled and that the measurements of regioselectivity are meaningful mechanistically.

The reactions of the halides with TBTH (and tri-n-butyltin deuteride, TBTD) were performed using azobis(isobutyronitrile), AIBN, as the initiator. Primary initiation was achieved photochemically (350 or 366 nm). The mechanism of such reductions using organosilicon carbon halides has been thoroughly studied.[21] The chain sequence involved is shown in eqns. 6-14, using α-1-Cℓ as an example.

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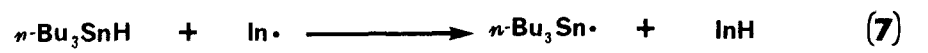


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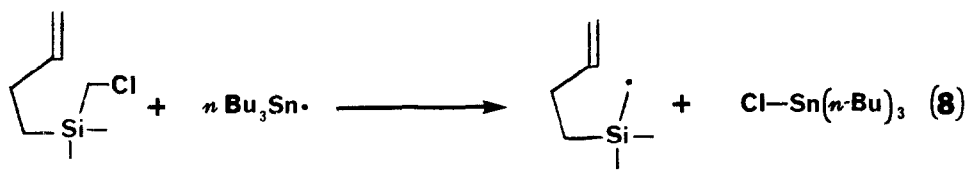


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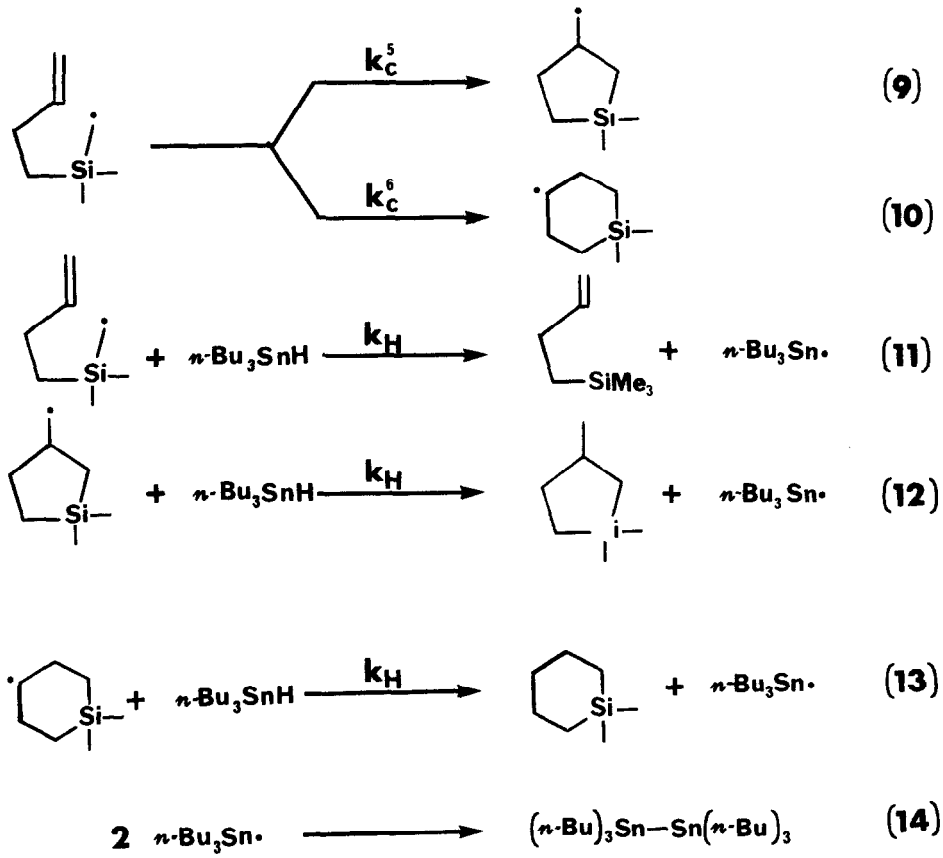



In terms of these mechanistic steps, regioselectivity is equal to $k_c^5/k_c^6$. The degree of cyclization is perhaps best quantified by the competition constant r, which equals $(k_c^5+k_c^6)/k_H$, and which was put into analytical form first by Rüchardt.[25] Its use in the present study is given in eqn. 15.

$$[\text{cyclized product}] = r\,\ell n\left[\frac{([TBTH] + r)}{r}\right] \qquad (15)$$

The study of these halides can thus be summarized as the determination of the value of the denoted rate constants in eqns. 9-13 relative to the parent 5-hexen-1-yl structure. In those studies using TBTD, the significant changes in the mechanism are the transfer steps (eqns. 11-13), for which the rate constant $k_D$ is also a matter of interest.

In Table 1 are given the results of the reactions of these halides with

TBTH (TBTD), together with literature data on the parent systems 5-bromo-1-hexene (1-Br) and 6-bromo-5,5-dimethyl-1-hexene (7-Br).

Table 1

Rearrangement (Cyclization) Data, 25°C

| [Halide]:[TBTH] | $[TBTH]_0$, M | % Cyclosilanes[a] | | $S^b$ | $10^3 r^c$, M |
|---|---|---|---|---|---|
| α-1-Cℓ | | 10 | 11 | | |
| 1:1.85 | 1.06 | 0.6 | 1.4 | 0.46±0.02 | 1.1 |
| 1:1.00 | 0.643 | 0.7 | 1.4 | | |
| 1:0.48 | 0.347 | 1.0 | 2.3 | | |
| 1:0.25 | 0.189 | 1.8 | 3.8 | | |
| 1:0.14 | 0.103 | 3.5 | 6.5 | | |
| 1:0.46[d] | 0.359 | 1.5 | 3.0 | 0.46±0.02 | 1.7 |
| 1:0.25[d] | 0.191 | 2.1 | 4.7 | | |
| 1:0.11[d] | 0.087 | 5.3 | 10.7 | | |
| β-1-Cℓ | | 10 | 11 | | |
| 1:2.13 | 2.36 | - | tr[e] | ∿ 0 | 0.67 |
| 1:1.05 | 1.04 | - | 0.8 | | |
| 1:0.559 | 0.550 | - | 1.4 | | |
| 1:0.331 | 0.330 | - | 1.5 | | |
| 1:0.198 | 0.200 | - | 2.8 | | |
| 1:0.582[d] | 0.588 | tr | 3.2 | ∿ 0 | 1.9 |
| 1:0.275[d] | 0.274 | tr | 5.8 | | |
| γ-1-Br | | 12 | 11 | | |
| 1:1.89 | 2.09 | 3.8 | 0.2 | 15±2 | 33 |
| 1:0.87 | 0.948 | 12.1 | 0.8 | | |
| 1:0.61 | 0.557 | 16.4 | 1.4 | | |
| 1:0.28 | 0.261 | 22.7 | 1.7 | | |
| 1:0.15 | 0.151 | 42.5 | 2.9 | | |
| 1:0.55[d] | 0.522 | 21.7 | 1.7 | 13±3 | 56 |
| 1:0.31[d] | 0.254 | 31.2 | 1.7 | | |
| 1:0.19[d] | 0.158 | 38.8 | 4.2 | | |
| 1-Br | | 2-H | 3-H | | |
| - [f] | 0.195 | 54.1 | 0.8 | 72±4 | 106 |
| - [f] | 0.093 | 69.1 | 0.9 | | |
| 7-Br | | 2′-H[g] | 3′-H[g] | | |
| - [f] | 1.39 | 70 | - [e] | > 100 | > 600[h] |
| - [f] | 1.00 | 77 | - [e] | | |
| - [f] | 0.20 | 94 | - [e] | | |

| | | | | |
|---|---|---|---|---|
| 17 | | 10 | - [i] | - [i] |
| 1:0.24 | 0.40 | ~ 100 | | |

[a]The remainder of the product in each case was the non-cyclized silane appropriate to each system. Yields were ~ quantitative based upon consumed halide. [b]Defined as regioselectivity and given by the average percentage yields of exo closure/endo closure products (i.e., $k_c^5/k_c^6$). [c]Defined as the competition constant and given by the ratio $(k_c^5+k_c^6)/k_H$. Its value was determined as described in the Experimental Section. [d]Tri-n-butyltin deuteride (TBTD) was used. [e]<0.1%. [f]Not available in the literature source of this data: 1-Br, ref. 3; 7-Br, ref. 20. [g]2-H=1,1,3-Trimethylcyclopentane; 3-H=1,1-Dimethyl cyclohexane. [h]Calculated by extrapolating the data in ref. 20 to 25°C. Activation parameters used to obtain $k_c^5$ ($1.6\times10^6 s^{-1}$) were: $\Delta H^{\ddagger}$ = 5.6 kcal $mol^{-1}$, $\Delta S^{\ddagger}$ = -11.4 eu, values derivable from the data reported. The value of $k_H$ used to calculate r was $2.4\times10^6$ $M^{-1}s^{-1}$ (ref. 4). [i]Meaningless in this case.

The data in Table 1 show clearly that significant differences in rearrangement (cyclization) behavior exist for the α- and β-organosilyl systems relative to their all-carbon parent. Moreover, these differences are reflected both in regioselectivity (the S values) and in cyclization propensity (the r values). Contrariwise, the γ-organosilyl system resembles the all-carbon parent much more closely. So the site, not the mere presence, of the silicon substituent is important and, curiously, not in a progressive manner. Of the three organosilyl systems studied, the β is the most unusual. Essentially no cyclization via the exo mode was observed in this system and the cyclization propensity was a hundred-fold less than for the parent system (1•)! As mentioned above, predictions about regioselectivity in the cyclization of 5-hexen-1-yl type radicals with non-carbon components can be risky. What is needed is a dissection of the data in Table 1 in terms of the rate constants $k_c^5$, $k_c^6$, and $k_{H(D)}$. An attempt to do this dissection for those radicals with available data is given in Table 2.

Table 2

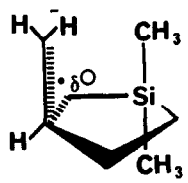
Rate Constant Data, 25°C

| Radical | $k_c^5(s^{-1})$[a] ($k_{rel}$) | $k_c^6(s^{-1})$[b] ($k_{rel}$) | $k_H(M^{-1}s^{-1})$[c] ($k_{rel}$) | $k_D(M^{-1}s^{-1})$[d] ($k_{rel}$) |
|---|---|---|---|---|
| 1• | $2.5\times10^5$ (1.0) | $3.5\times10^3$ (1.0) | $2.4\times10^6$ (1.0) | $1.2\times10^6$ (1.0) |
| 7• | $4.7\times10^6$[e] (19) | - [f] | $3.6\times10^6$[e] (1.5) | - [g] |
| α-1• | $6.6\times10^3$ (0.03) | $1.4\times10^4$ (4.0) | $1.9\times10^7$ (7.9) | $1.2\times10^7$ (10) |
| γ-1• | $6.5\times10^4$ (0.3) | $4.3\times10^3$ (1.2) | $2.1\times10^6$ (0.9) | $1.2\times10^6$ (1.0) |

[a]Calculated from $k_c^5=(S/S+1)\cdot r\cdot k_H$. [b]Calculated from $k_c^6=k_c^5/S$. [c]Differences between primary and secondary radicals have been ignored. The value for 1• is taken from ref. 4. The value for 7• is taken from data graciously communicated to the author by Dr. K. U. Ingold. The values for α-1• and γ-1• are taken from the author's study of $(CH_3)_3SiCH_2$• and $(CH_3)_3SiCH_2CH_2CH_2$• with TBTH (to be published with Dr. Ingold and coworkers at a later date). [d]Calculated from $k_D=(k_c^5+k_c^6)/r$ for α-1• and γ-1•. The value for 1• is from ref. 4. [e]Calculated from data supplied by Dr. K. U. Ingold. [f]No *endo* cyclization observed. [g]Not available.

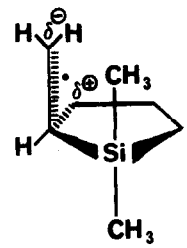
Notable for its absence in Table 2 is the β-1• radical. At present no value for $k_H$ is available in this case, so no definitive mechanistic conclusions are possible.[26] Some speculative comment will be made later. But for the α- and γ-systems, dissection of the data in Table 1 as shown in Table 2 reveals that the unusual behavior of the α-system is caused by two phenomena. First, the rate of hydrogen abstraction in chain transfer with TBTH and TBTD is an order of magnitude faster than for the parent 1• radical.[27] This fast process obviously lowers the cyclization propensity for the α-system and accounts for the small r value observed. Second, an abnormally low value for *exo* cyclization, coupled with an essentially "normal" value for *endo* cyclization, accounts for the reversed regioselectivity observed. As a further point of interest, the dissected data reveal the similar behavior of the γ- and parent all-carbon systems. Their kinetic values are essentially identical, albeit *exo* cyclization in γ-1• is somewhat slower than in 1• itself.[28] The slower $k_c^5$ values for α-1• and γ-1• are believed from inspection of scale models to result from the less favorable geometry for *exo* ring closure in these cases, a result arising from the longer Si-C bonds present *anywhere* in the chain, which increases the strain present in the incipient

five-membered ring. Additionally, if 4 does in fact accurately resemble the transition state for radical additions to a double bond, then the reduced $k_c^5$ value for α-1• relative to γ-1• may be rationalized as well.[29] α-Silyl carbon-centered radicals engage most readily in processes where incremental negative charge can be centered on the carbon center.[17] This is, in fact, the opposite of 4 and may rationalize the low $k_c^5$ rate constant observed for α-1•. This polar factor would not be operative for γ-1•. These considerations are shown in structures 18 and 19.




18

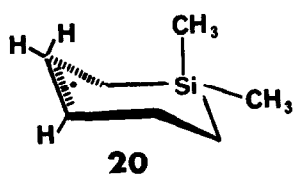
EXO CYCLIZATION IN α—1•




19

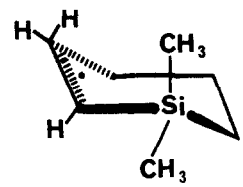
EXO CYCLIZATION IN γ—1•

Endo addition, on the other hand, would seemingly involve less dipolar character than 4 because the dipole would require a less stable secondary carbanion component. Hence, with both α- and γ-1•, the sterically easier endo addition would be comparable in rate for each, as shown in the sterically similar structures 20 and 21, with little change development in either case.




20

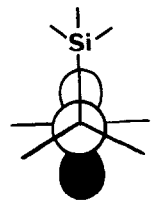
ENDO CYCLIZATION IN α—1•




21

ENDO CYCLIZATION IN γ—1•

Lastly, some speculation about the curious behavior of β-1•. Cyclization is difficult in this system, and exo cyclization is virtually absent. One factor possibly involved is the known synperiplanar conformational preference for such radicals[30], shown in 22,




**22**

where the C-Si bond bisects the half-occupied p orbital of the carbon radical center, i.e., the Si-C-C bonds lie in one plane. Any cyclization, exo or endo, requires that this conformation be changed to an approximate gauche relationship, a change that may be resisted[31] and lower the cyclization propensity. Add to this the previous disadvantage of exo to endo cyclization caused by the longer Si-C bonds present and the near absence of the 10 among the products from β-1-Cℓ may be further rationalized. A view that the unusual behavior of β-1• might be the result of the scission shown in eqn. 16 is not tenable, because β-1-H was formed in high yield.


**(16)**

Until the hydrogen abstraction value $k_H$ is determined, however, no definitive mechanistic conclusions can be drawn. Work continues to establish this value.

## Experimental Section

Spectra were recorded in the usual fashion. $^1$H NMR chemical shifts are given in δ values relative to TMS at δ 0.0. Only structurally significant IR absorptions are listed. Microanalyses were performed by Micro-Tech Laboratories, Skokie, IL.

6-Chloro-5,5-dimethyl-5-sila-1-hexene (α-1-Cℓ) was prepared by a literature

method[23]; colorless oil, bp 73-74°C at 13 mm, lit.[23] bp 70-73°C at 17 mm. The $^1$H NMR spectrum matched that reported.[23] Material used in the study was collected by GLPC (SE-30, 135°).

6-Chloro-4,4-dimethyl-4-sila-1-hexene (β-1-Cℓ). (Chloromethyl)allyldimethylsilane (8) was synthesized by a reported method.[23] While the colorless oil had its IR and $^1$H NMR spectra identical with those published[23], its bp was 45.5-46°C at 15 mm, lit.[23] 42-47°C at 1 mm. By comparison with α-1-Cℓ, the present bp seems more reasonable. Reaction of 8 (8.0 g, 54 mmoles) with magnesium (1.31 g, 54 mg-atoms) in dry ether under nitrogen afforded the Grignard reagent. Formaldehyde gas (generated from paraformaldehyde at 180-195°C) was passed along with nitrogen into the vigorously stirred Grignard reagent solution at 0°C. When no further absorption was evident (consumption of 3 g of paraformaldehyde), the solution was added carefully to ice (200 mL). The solids present were dissolved by addition of saturated ammonium chloride solution. The product was taken up in ether, washed, and dried. The ether was removed and the residual oil was distilled in a Hickman still at 85°C and 4 mm.

3,3-Dimethyl-3-sila-5-hexen-1-ol (9) was obtained as a colorless oil, 4 g (51%); δ ($CCℓ_4$) 5.6 (m, 1H, -CH=$CH_2$), 4.9, 4.6 (2m, 2H, -CH=$CH_2$), 3.6 (t, J=8Hz, 2H, -$CH_2$O), 2.2 (br s, conc. dependent, 1H, OH), 1.5 (d, J=8Hz, 2H, 4-$CH_2$), 0.9 (t, J=8Hz, 2H, 2-$CH_2$), 0.0 (s, 6H, Si($CH_3$)$_2$); ν (neat) 3600-3200 (OH), 3100, 1640 (C=C), 1260, 850-820 (Si($CH_3$)$_2$).

Anal. Calcd for $C_7H_{16}$OSi:C, 58.27; H, 11.18.
Found: C, 57.68; H, 11.13.

Reaction of alcohol 9 with thionyl chloride in pyridine led to poor results, so 2,2,6,6-tetramethylpiperidine (TMP) was substituted for pyridine. Alcohol 9 (4.0 g, 27.6 mmoles) and TMP (Aldrich, 4.0 g, 28.4 mmoles) in dry ether (60 mL) was added to thionyl chloride (3.44 g, 28.8 mmoles) in dry ether (50 mL) with stirring at 25°C. When the vigorous initial reaction subsided, the solution was refluxed for 5 h. The precipitated salt (98%) was filtered and the ether removed. The residual yellow oil was distilled in a Hickman apparatus at 70°C and 9 mm to afford β-1-Cℓ as a colorless oil, 3.1 g (69%); δ ($CCℓ_4$) 5.6 (br m, 1H, -CH=$CH_2$), 4.9, 4.6 (2 m, 2H, -CH=$CH_2$), 3.6 (t, J=8Hz, 2H, -$CH_2$Cℓ), 1.5 (d, J=8Hz, 2H, 5-$CH_2$), 1.2 (m, 2H, 3-$CH_2$), 0.06 (s, 6H, Si($CH_3$)$_2$); ν (neat) 3100, 1640 (C=C), 1260, 830-810 (Si($CH_3$)$_2$).

Anal. Calcd for $C_7H_{15}$CℓSi:C, 51.66; H, 9.29.
Found: C, 51.07; H, 9.53.

The chloride decomposed readily upon attempted purification by GLPC > 100°C on SE-30 columns.[32] Material collected at 75°C from a Carbowax 20M column was used in the study.

6-Bromo-3,3-dimethyl-3-sila-5-hexene (γ-1-Br). Vinylmagnesium bromide in THF (Alfa, 1.4 M, 40 mL, 56 mmoles) was added dropwise under nitrogen at 25°C to a stirred solution of freshly distilled 3-bromopropyltrichlorosilane (Petrarch, 14.1 g, 55 mmoles) in dry ether (100 mL). When the addition was completed, the solution was refluxed for 72 h. The material was then cooled, diluted with further ether (100 mL), and treated similarly with methylmagnesium bromide in ether (Aldrich, 3M, 37 mL, 111 mmoles). When this addition had been made, the

mixture was refluxed for another 48 h. The chilled material was processed by addition of hydrochloric acid (10%) and subsequent standard washes. The residual oil was characterized as a mixture of γ-1-Br and 3-bromopropyltrimethylsilane. Distillation was ineffective at their separation, so γ-1-Br was collected by GLPC (SE-30, 125°C), 3 g, 26%; δ ($CDCl_3$) 6.3-5.4 (br m, $-CH=CH_2$), 3.4 (t, J=7Hz, 2H, $-CH_2Br$), 1.8 (br m, 2H, 5-$CH_2$), 0.7 (br m, 2H, 4-$CH_2$), 0.07 (s, 6H, $Si(CH_3)_2$); ν (neat) 3100, 1600 (C=C), 1260, 850-820 $cm^{-1}$.

Anal. Calcd for $C_7H_{15}BrSi$:C, 40.58; H, 7.30.
Found: C, 40.07; H, 7.20.

Preparation of Silane Products. 5,5-Dimethyl-5-sila-1-hexene (α-1-H) was prepared as reported by Connolly and Fryer.[23] Its IR and $^1H$ NMR spectra agreed with those reported.

4,4-Dimethyl-4-sila-1-hexene (β-1-H) was prepared from allyldimethylchlorosilane (Petrarch) and ethylmagnesium bromide (Aldrich), bp 114-118°C, lit.[33] bp 116°C (made by an alternative route); δ ($CCl_4$) 5.7 (br m, 1H, $-CH=CH_2$), 4.9, 4.6 (2 m, 2H, $-CH=CH_2$), 1.8 (d, J=6Hz, 2H, 2-$CH_2$), 0.93 (m, 3H, C-$CH_3$), 0.56 (m, 2H, 5-$CH_2$), 0.01 (s, 6H, $Si(CH_3)_2$). Material used for GLPC analytical studies was collected by GLPC (SE-30, 95°C). 3,3-Dimethyl-3-sila-1-hexene (γ-1-H) was obtained by GLPC collection of the reduction products of γ-1-Br (SE-30, 80°C), micro bp 111-113°C, lit.[34] bp 112-113°C (made by another route); δ ($CDCl_3$) 6.1-5.2 (br m, 3H, $-CH=CH_2$), 1.9-0.23 (br m, 7H, $-CH_2CH_2CH_3$), 0.0 (s, 6H, $Si(CH_3)_2$). 1,1,3-Trimethyl-1-silacyclopentane (10) was prepared by catalytic hydrogenation of 1,1,3-trimethyl-1-sila-3-cyclopentene in hexane as reported[35], bp 120-122°C, lit.[35] 120-123°C; δ ($CCl_4$) 1.7 (br m, 3H, 3-CH and 4-$CH_2$), 0.9 (d, J=6Hz, 3H, C-$CH_3$), 1.1-0.3 (br m, 4H, 2, 5-$CH_2$'s), 0.0 (s, 6H, $Si(CH_3)_2$); ν (neat) 1380 (C-$CH_3$), 1260, 850, 810 ($Si(CH_3)_2$) $cm^{-1}$. The material used in the study was collected by GLPC (SE-30, 85°C). 1,1,2-Trimethyl-1-silacyclopentane (12) and 1,1-dimethyl-1-silacyclohexane (11) were synthesized by Pt(VI)-promoted cyclization of 6,6-dimethyl-6-sila-1-hexene as reported.[36] The ratio of 12:11 was 83:17 (lit.[36] ratio 90:10). Silacyclopentane 12 was separated from 11 by GLPC (SE-30, 80°C). Its spectral properties agreed with those reported.[36] Though quite similar, the $^1H$ NMR chemical shift differences of the Si-$CH_3$ resonances in 10 and 12 deserve brief comment. In 10 the stereoisomeric $CH_3$ groups on silicon are just barely distinguishable; in 12 their chemical shifts are readily discernible ($\Delta\delta \sim 3Hz$). This difference is undoubtedly due to the closer proximity of the C-$CH_3$ to the $Si(CH_3)_2$ in 12 compared to 10. For the study described herein, the silacyclohexane 11 used was purchased material (petrarch), rather than the minor component of the above misture. Sequence used to Prepare 3-Bromomethyl-1,1-dimethyl-1-silacyclopentane (17).

Diethyl (4-chloro-3,3-dimethyl-3-sila-1-butyl)propanedioate (13). To a stirred volume of diethyl malonate (Fisher, 303 mL, 320 g, 2 moles) at 150°C under nitrogen was added (1 drop/5 sec) a solution of (chloromethyl)vinyldimethylsilane (Petrarch, 13.5 g, 100.2 mmoles) and di-t-butyl peroxide (Shell, 3 g, 20.5 mmoles). After the addition the solution was held at 150°C for another hour. The excess diethyl malonate was removed (bp 102° at 46 mm) until the pot temperature reached 160°C. The residual oil was further distilled in a Kugelrohr oven to afford

more diethyl malonate (total recovery 87.5%) and colorless ester 13 at 0.5 mm and a bath temp. of 122°C, 17.6 g (60%); δ ($CDC\ell_3$) 4.2 (q, J=7Hz, 4H, $-OCH_2$), 3.3 (t, J=4Hz, 1H, $-CH(COOEt)_2$), 2.8 (s, 2H, $-CH_2C\ell$), 1.8 (br m, 2H, $-CH_2CH(COOEt)_2$), 1.2 (t, J=7Hz, 6H, $-OCH_2CH_3$), 0.6 (m, 2H, $CH_2$-Si), 0.06 (s, 6H, $Si(CH_3)_2$); ν (neat) 1750, 1715 (CO), 1375 (C-$CH_3$), 1300-1140, 1040, 855 $cm^{-1}$.

Anal. Calcd for $C_{12}H_{23}O_4C\ell Si$: C, 48.88; H, 7.86.
Found: C, 49.36; H, 8.24.

Diethyl-1,1-dimethyl-1-silacyclopentane-3,3-dicarboxylate (14). To a solution of freshly made sodium ethoxide in ethanol (26.1 mmole in 475 mL), stirred at reflux under nitrogen, was added dropwise a solution of ethanol and ester 13 (7.4 g, 25.1 mmoles). The system was arranged such that the ester was added slowly (1 drop/15 sec) to the ethanol (75 mL), itself contained in an addition funnel situated to receive both ester 13 and the condensate from the refluxing sodium ethoxide solution. The rate of addition from this funnel was adjusted so that ∿ 75 mL remained in it throughout the addition. The addition of 13 took 3½ h. After an additional hour under reflux, the cooled solution was treated with water (100 mL). The material was extracted with ether and processed by the usual washes. The dried extracts were stripped and the residual oil distilled (Kugelrohr) at 85°C and 0.35 mm. Ester 14 was obtained as a pleasant-smelling colorless oil, 4.6 g (71%); δ ($CDC\ell_3$) 4.09 (q, J=7Hz, 4H, $-OCH_2$), 2.1 (t, J=7Hz, 2H, 4-$CH_2$), 1.2 (t, J=7Hz, 6H, $-OCH_2CH_3$), 1.0 (s, 2H, 2-$CH_2$), 0.53 (t, J=7Hz, 2H, 5-$CH_2$), 0.03 (s, 6H, $Si(CH_3)_2$); ν (neat) 1750, 1715 (CO), 1375 (C-$CH_3$), 1250, 1170, 1110, 1060, 960, 860 ($Si(CH_3)_2$) $cm^{-1}$.

Anal. Calcd for $C_{12}H_{22}O_4Si$: C, 55.78; H, 8.58.
Found: C, 55.44; H, 9.08.

Ethyl 1,1-dimethyl-1-silacyclopentane-3-carboxylate (15). Diester 14 was decarboethoxylated using lithium chloride in dimethylsulfoxide containing an equivalent of water, following the general directions of Krapcho and co-workers.[37] Ester 15 was prepared several times by this method and usually some unchanged 14 accompanied it. Yields were high (∿ 90%), but conversions ranged from 32-80%. The reaction seemed capricious. In any event, colorless 15 was eventually obtained, bp (Kugelrohr) 80°C at 0.7 mm; δ ($CDC\ell_3$) 4.06 (a quartet doubleted, $A_3XY$ system, $J_{AX}$=7Hz, $J_{XY}$=3Hz, 2H, $-OCH_2CH_3$), 2.6-1.3 (br m, 3H, H-3, 4-$CH_2$), 1.1 (t, J=7Hz, 3H, $-OCH_2CH_3$), 1.1 (m, 2H, 2-$CH_2$), 0.56 (m, 2H, 5-$CH_2$), 0.41 (s, 3H, Si-$CH_3$), 0.35 (s, 3H, Si-$CH_3$); ν (neat) 1715 (CO), 1380 (C-$CH_3$), 1260, 850 ($Si(CH_3)_2$) $cm^{-1}$.

Anal. Calcd for $C_9H_{18}O_2Si$: C, 58.01; H, 9.74.
Found: C, 57.56; H, 9.48.

3-Hydroxymethyl-1,1-dimethyl-1-silacyclopentane (16). Reduction of ester 15 to this alcohol[38] was achieved in typical fashion using lithium aluminum hydride in ether; colorless oil, bp (Kugelrohr) 85°C at 0.7 mm, 75%; δ ($CDC\ell_3$) 3.5 (d, J=7Hz, 2H, $-CH_2O$), 2.1 (s, exchangeable, 1H, -OH), 2.1-1.3 (br m, 3H, H-3, 4-$CH_2$), 1.2-0.13 (br m, 4H, 2, 5-$CH_2$'s), 0.0 (s, 6H, $Si(CH_3)_2$); ν (neat) 3400-3200 (OH), 1250, 1060, 1010, 850-810 ($Si(CH_3)_2$) $cm^{-1}$.

Anal. Calcd for $C_7H_{16}OSi$: C, 58.27; H, 11.18.
Found: C, 57.97; H, 11.35.

3-Bromomethyl-1,1-dimethyl-1-silacyclopentane (17). Conversion of alcohol 16 to bromide 17 using $PBr_3$ in methylene chloride was marred by apparent rearrangement and/or degradation. Therefore, alcohol 16 was converted to its tosylate with tosyl chloride in pyridine (72 h at 4°C) in standard fashion. The oily tosylate (2.2 mmole) was not isolated, but rather was heated with lithium bromide (3.62 mmole) in purified acetone (15 mL) under reflux for 20 h. The solution was filtered and freed of solvent. The residual oil was distilled in a Hickman still (90°C, 35 mm) to give bromide 17 as a colorless oil, 52% from alcohol 16, with a penetrating odor; δ ($CDC\ell_3$) 3.4 (dd, AXY, $J_{AX}$=7Hz, $J_{AY}$=6Hz, $J_{XY}\simeq$ 2 Hz, 2H, $-CH_2Br$), 2.5-1.6 (br m, 3H, H-3, 4-$CH_2$), 1.4-0.23 (br m, 4H, 2, 5-$CH_2$'s), 0.03 (s, 6H, $Si(CH_3)_2$); ν (neat) 1260, 1240, 860, 810 ($Si(CH_3)_2$). The bromide decomposed upon attempted re-distillation or collection by GLPC. Its structure is based upon its spectra and formation of 10 upon treatment with TBTH.

Reaction of Halides with TBTH (TBTD). The reductions were performed in NMR tubes. All weights were recorded to the nearest mg. Separate tubes were filled with the appropriate halide (∿ 0.5 mmole), freshly distilled TBTH (or TBTD), (varying amounts to establish certain halide: TBTH(D) ratios; cf. Table 1), nonane (∿ 0.5 mmole, internal GLPC standard) and AIBN (∿ 0.05 mmole, initiator). Hexadecane (Aldrich) was then added as an inert solvent to bring all the solutions to a total volume of 0.50 mL. The solutions were purged with nitrogen for one minute, capped, and then exposed to irradiation (366 nm or 350 nm) in a merry-go-round Rayonet minireactor for an appropriate time (NMR absence of TBTH), usually 3 h. Further irradiation (to 7 h) had no effect on the reaction. Known mixtures of all components (reactants and products) were subjected to GLPC with nonane as an internal standard to determine GLPC response factors. All data in Table 1 are derived using such factors. The irradiated reaction material was analyzed by GLPC on an SE-30 column at an appropriate temperature for maximum separation of peaks. Peak identity was made by "spiking" the mixtures with knowns. Peak areas were determined by the cut-and-weigh technique. The competition constant r was evaluated by an iterative computer program. Mass balances were uniformly >93%. Unreacted halide was accounted for; only in those cases where the TBTH was in excess was the addition of TBTH to the double bond of the product(s) noted. Such runs were not included in the determination of r values.

## Acknowledgement

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15. This work is of interest for another reason. The substrates used were β-oxa-α-silyl carbon halides, which cyclized preferentially in the exo (orthodox) mode. This stands in marked contrast to the present study of α-silyl carbon halide cyclization, where the endo mode is favored. Clearly, the regioselectivity of the cyclization remains a confusing (but challenging) issue.

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26. Work on this point is in progress.

27. Discussion of this unusual result will be reserved for a forthcoming publication with K. U. Ingold and J. Lusztyk.

28. The augmented value of $k_c^5$ for 7• has been discussed.[20]

29. Ingold's view[11] ascribed the difference in α- vs. γ-cyclization to a more serious steric crowding for exo closure in α-1• caused by the position of the dimethylsilyl function. The models used by the author showed no obvious difference in this regard for the α and γ cases.

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31. Note that $(CH_3CH_2)_3Si\text{-}CH_2CH_2\bullet$ has a rotational barrier of 1.2 kcal $mol^{-1}$, some 0.7-0.8 kcal higher than that for the n-propyl radical: Fischer, H.; "Free Radicals", Kochi, J. K., editor, Wiley, New York, N.Y., 1973, Vol. 2, Chapter 19, p. 483.

32. Attempts to prepare the corresponding bromide gave a visibly unstable product which readily evolved ethylene and formed allyldimethylbromosilane.

33. Mironov, V. F.; Pogononkina, N. A.; Izv. Akad. Nauk SSSR, Ser. Khim., 1959, 85.

34. Nametkin, N. S.; Durgar'yan, S. G.; Chemyakov, I. E.; Izv. Akad. Nauk SSSR, Ser. Khim., 1970, 1181.

35. Araki, T.; Terunuma, D.; Fuse, T.; Bull. Chem. Soc. Jap., 1972, 45, 293. The solvent choice is important; use of methanol (or ethanol as in this Laboratory) led to ring-opening.

36. Swisher, J. V.; Chen. H.-H.; J. Organometal. Chem., 1974, 69, 83.

37. Krapcho, A. P.; Weimaster, J. F.; Eldridge, J. M.; Jahngen, Jr., E. G. E.; Lovey, A. J.; Stephens, W. P.; J. Org. Chem., 1978, 43, 138.

38. The alcohol was reported earlier as a component in a mixture of isomers, but no structural information was given: Manuel, G.; Mazerolles, P.; Florence, J.-C., J. Organometal. Chem., 1971, 30, 5.