Note Added in Proof. The Birch reduction of the 1-methyl derivative of **6** was found to proceed smoothly without adding TMS-Cl or HMDS to give the corresponding *N*-methyl derivative of **7** in excellent yield.

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Supplementary Material Available: General methods, sources of materials, and the NOESY spectrum of **6** (2 pages). Ordering information is given on any current masthead page.

Absolute Rate Constants for Some Intermolecular and Intramolecular Reactions of α-, β-, and γ-Silicon-Substituted Radicals[1]

James W. Wilt,[2a] J. Lusztyk,[3] Mehoob Peeran,[2b] and K. U. Ingold*[3]

Contribution from the Department of Chemistry, Loyola University of Chicago,
Chicago, Illinois 60025, and the Division of Chemistry, National Research Council of Canada,
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Abstract: Rate constants for hydrogen atom abstraction from n-Bu_3GeH (k^{GeH}) by $Me_3SiCH_2^{\bullet}$ ($\mathbf{1}^{\bullet}$), $Me_3SiCH_2CH_2^{\bullet}$ ($\mathbf{2}^{\bullet}$), and $Me_3SiCH_2CH_2CH_2^{\bullet}$ ($\mathbf{3}^{\bullet}$) and from n-Bu_3SnH (k^{SnH}) by $\mathbf{1}^{\bullet}$ and $\mathbf{3}^{\bullet}$ have been determined at ambient temperatures. The order of decreasing radical reactivity is $\mathbf{1}^{\bullet} > n\text{-alkyl} > \mathbf{3}^{\bullet} > \mathbf{2}^{\bullet}$. However, for bromine abstraction from the parent bromides by n-$Bu_3Sn^{\bullet}$ and n-$Bu_3Ge^{\bullet}$, the order of decreasing reactivity is **1-Br** > **2-Br** > **3-Br** ~ n-alkyl bromide. The Arrhenius equations for reaction of $\mathbf{1}^{\bullet}$ and $\mathbf{3}^{\bullet}$ with n-Bu_3SnH were also determined: $\log (k^{SnH}(\mathbf{1}^{\bullet})/(M^{-1}\ s^{-1})) = (10.2 \pm 0.5) - (3.90 \pm 0.62)/\theta$ and $\log (k^{SnH}(\mathbf{3}^{\bullet})/(M^{-1}\ s^{-1})) = (8.4 \pm 0.7) - (2.81 \pm 0.95)/\theta$, where $\theta = 2.3RT$ kcal/mol. These kinetic data are discussed in relation to previously measured[8] rate constant ratios, k_c^{5+6}/k^{SnH} and k_{exo}^5/k_{endo}^6, where k_c^{5+6} corresponds to the cyclization of α-, β-, and γ-dimethylsilyl-substituted 5-hexenyl radicals to form 5-membered (k_{exo}^5) and 6-membered (k_{endo}^6) silacycloalkylmethyl radicals.

The growing popularity of free-radical cyclization for the construction of ring systems can be partly attributed to their predictability. That is, provided the cyclization is under kinetic control the size of the ring that will be formed predominantly can be forecast by the Baldwin–Beckwith rules.[4] Few exceptions to these rules are known and even fewer have received detailed study.

The best known illustration of the Baldwin–Beckwith rules is provided by the contrathermodynamic 5-exo cyclization of the 5-hexenyl radical to cyclopentylmethyl rather than the thermodynamically preferred, 6-endo cyclization to the cyclohexyl radical[7] ($k_{exo}^5/k_{endo}^6 = 72$ at 25 °C).[8] There are innumerable variants of this reaction[7] with k_{exo}^5/k_{endo}^6 values that are generally at least as great as for 5-hexenyl and in which the new 5-membered ring contains substituents (including a second, fixed ring) or in which the ring contains heteroatoms from the first row of the periodic table (i.e., O and N). By and large, exceptions to the Baldwin–Beckwith rules arise when an atom from the second row is incorporated into the new ring.[8-11] For example, one of us has reported[8] that the replacement of a CH_2 group at the 2 (α), 3 (β), or 4 (γ) position of 5-hexenyl by an $SiMe_2$ group gave quite unexpected results, both in terms of exo/endo product ratios[10] and in terms of the *apparent* rates of cyclization of these three radicals. The standard experimental approach was followed in which an acyclic parent halide was reacted with n-Bu_3SnH under radical-chain conditions. Cyclization of the acyclic radical (rate constant, $k_c^{5+6} = k_{exo}^5 + k_{endo}^6$) competes with hydrogen atom abstraction from the tin hydride (rate constant k^{SnH}); see Scheme I for the competitive reactions of the α-dimethylsilyl-substituted radical. The results obtained[8] with the three $SiMe_2$-substituted radicals and with two all-carbon analogues are summarized in Table I. For the latter, values of k^{SnH} are known[12,13] and hence k_{exo}^5 and k_{endo}^6 can be calculated. However, values of k^{SnH} for the silicon-containing radicals are not known and therefore it was uncertain as to whether the different behavior of these radicals, relative to the behavior of the all-carbon radicals, was due to differences in their rates of attack on n-Bu_3SnH. In the present paper, we have resolved this uncertainty by determining values of k^{SnH} for $\mathbf{1}^{\bullet}$, $\mathbf{2}^{\bullet}$, and $\mathbf{3}^{\bullet}$, which are appropriate analogues for the α-, β-, γ-dimethylsilyl-substituted 5-hexenyl radicals.

$Me_3SiCH_2^{\bullet}$	$Me_3SiCH_2CH_2^{\bullet}$	$Me_3SiCH_2CH_2CH_2^{\bullet}$
$\mathbf{1}^{\bullet}$	$\mathbf{2}^{\bullet}$	$\mathbf{3}^{\bullet}$

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[2] Loyola. (a) Died: May 13, 1987. To whom this paper is dedicated. (b) Present address: Department of Chemistry, St. Joseph's College, Bangalore-560001, India.

[3] NRCC.

[4] First advanced by Beckwith[5] and later supported by Baldwin.[6]

[5] Struble, D. L.; Beckwith, A. L. J.; Gream, G. E. *Tetrahedron Lett.* **1968**, 3701–3704. Beckwith, A. L. J.; Gream, G. E.; Struble, D. L. *Aust. J. Chem.* **1972**, *25*, 1081–1105.

[6] Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–736.

[7] For reviews, see: (a) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, Essay 4. (b) Surzur, J. M. *React. Intermed. (Plenum)* **1981**, *2*, 121–295. (c) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3071–3100.

[8] Wilt, J. W. *Tetrahedron* **1985**, *41*, 3979–4000.

[9] (a) Chatgilialoglu, C.; Woynar, H.; Ingold, K. U.; Davies, A. G. *J. Chem. Soc., Perkin Trans. 2* **1983**, 555–561. (b) Barton, T. J.; Revis, A. *J. Am. Chem. Soc.* **1984**, *106*, 3802–3805.

[10] Systems containing the $C{=}CCH_2OSiMe_2CH_2^{\bullet}$ moiety also undergo preferential 6-endo cyclization. See, e.g.: Nishiyama, H.; Kitajima, T.; Matsumoto, M.; Itoh, K. *J. Org. Chem.* **1984**, *49*, 2298–2300. Koreeda, M.; George, I. A. *J. Am. Chem. Soc.* **1986**, *108*, 8098–8100.

[11] Bastien, G.; Surzur, J. M. *Bull. Soc. Chim. Fr.* **1979**, 601–605. Bastien, G.; Crozet, M. P.; Flesia, E.; Surzur, J. M. *Ibid.* **1979**, 606–613.

[12] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742.

[13] Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594–4596.

0002-7863/88/1510-0281$01.50/0

Scheme I

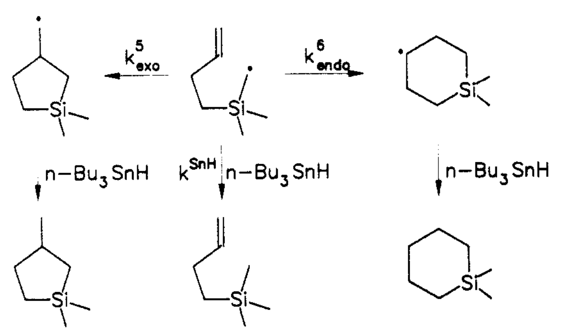

Table I. Summary of Kinetic Data Reported in Ref 8 for the Cyclization of 5-Hexenyl and Some Substituted 5-Hexenyl Radicals at 25 °C

radical	$k^5_{\text{exo}}/k^6_{\text{endo}}$	$10^3k_c^{5+6}/k^{\text{SnH}}$, M
$CH_2{=}CHCH_2CH_2SiMe_2CH_2^{\bullet}$	0.46	1.1
$CH_2{=}CHCH_2SiMe_2CH_2CH_2^{\bullet}$	~0	0.67
$CH_2{=}CHSiMe_2CH_2CH_2CH_2^{\bullet}$	15	33
$CH_2{=}CHCH_2CH_2CH_2CH_2^{\bullet}$	72	106
$CH_2{=}CHCH_2CH_2CMe_2CH_2^{\bullet}$	>100	>600

Table II. Arrhenius Parameters and Rate Constants at 27 °C for Reaction of Some Carbon-Centered Radicals with n-Bu_3SnH[a]

radical	log $(A/(M^{-1}\ s^{-1}))$	E, kcal/mol	$10^{-6}k^{\text{SnH}}$, $M^{-1}\ s^{-1}$
$Me_3SiCH_2^{\bullet}$[b]	10.2 ± 0.5	3.90 ± 0.62	$22._4$
$Me_3SiCH_2CH_2CH_2^{\bullet}$[c]	8.4 ± 0.7	2.81 ± 0.95	2.2_1
$CH_3^{\bullet}$[d]	9.39 ± 0.28	3.23 ± 0.34	$10._6$
n-alkyl[d,e]	9.07 ± 0.24	3.69 ± 0.32	2.4_0

[a] Errors correspond to 95% confidence limits but include only random errors. [b] Generated from the arsine in isooctane and in benzene as solvent at temperatures from −1 to +62 °C. [c] Generated from the peroxide in *tert*-butylbenzene as solvent at temperatures from −20 to +35 °C. [d] Data are from ref 12. [e] Combined data for the ethyl and *n*-butyl radicals.

Results

Direct Measurement of k^{SnH} for $Me_3SiCH_2^{\bullet}$ (1•). This radical was produced by reaction of photochemically generated *tert*-butoxyl radicals with tris[(trimethylsilyl)methyl]arsine: EPR

$$Me_3COOCMe_3 \xrightarrow{h\nu} 2Me_3CO^{\bullet} \tag{1}$$

$$Me_3CO^{\bullet} + (Me_3SiCH_2)_3As \rightarrow (Me_3SiCH_2)_3\dot{A}sOCMe_3 \tag{2}$$

$$(Me_3SiCH_2)_3\dot{A}sOCMe_3 \rightarrow \underset{\mathbf{1}}{Me_3SiCH_2^{\bullet}} + (Me_3SiCH_2)_2AsOCMe_3 \tag{3}$$

spectrum, $a^{H_\alpha}(2H) = 20.75$ G, $a^{H_\gamma}(9H) = 0.43$ G at 25 °C; lit.[14] $a^{H_\alpha}(2H) = 20.88$ G, $a^{H_\gamma}(9H) = 0.41$ G at −126 °C. Laser flash photolysis of these two reagents[15] with added n-Bu_3SnH was carried out as described previously[12,13] and growth of the n-$Bu_3Sn^{\bullet}$ radical was monitored at 400 or 450 nm. Rate constants for

$$Me_3SiCH_2^{\bullet} + n\text{-}Bu_3SnH \xrightarrow{k^{\text{SnH}}(1^{\bullet})} Me_4Si + n\text{-}Bu_3Sn^{\bullet} \tag{4}$$

reaction 4 were measured in isooctane and in benzene as solvent over the temperature range −1 to +62 °C (see Supplementary Material). They yielded the Arrhenius parameters given in Table II.

Direct Measurement of k^{SnH} for $Me_3SiCH_2CH_2CH_2^{\bullet}$ (3•). The corresponding trisubstituted arsine reacted with photochemically generated *tert*-butoxyl radicals to yield the expected radical, 3•: EPR spectrum, $a^{H_\alpha}(2H) = 21.75$ G, $a^{H_\beta}(2H) = 27.15$ G at 25 °C.[17] Unfortunately, laser flash photolysis of the peroxide and arsine produced a transient ($\lambda_{\max} = 380$ nm) which prevented measurement of the rate constant for reaction of *tert*-butoxyl with the arsine and also made it quite impossible to monitor growth of the n-$Bu_3Sn^{\bullet}$ radical upon the addition of n-Bu_3SnH. This 380-nm transient was produced even when using the arsine after purification by preparative GC. For this reason, 4-(trimethylsilyl)-*n*-butyryl peroxide was synthesized and, on photolysis, was shown by EPR spectroscopy to yield the desired radical, 3•. The

$$(Me_3SiCH_2CH_2CH_2CO_2)_2 \xrightarrow{h\nu} \underset{\mathbf{3}^{\bullet}}{2Me_3SiCH_2CH_2CH_2^{\bullet}} + 2CO_2 \tag{5}$$

peroxide was sufficiently stable toward n-Bu_3SnH for laser flash photolysis experiments to be carried out. The growth of the n-$Bu_3Sn^{\bullet}$ radical was monitored in the usual way. Kinetic

$$Me_3SiCH_2CH_2CH_2^{\bullet} + n\text{-}Bu_3SnH \xrightarrow{k^{\text{SnH}}(3^{\bullet})} Me_3SiCH_2CH_2CH_3 + n\text{-}Bu_3Sn^{\bullet} \tag{6}$$

measurements in *tert*-butylbenzene, made over the temperature range −20 to +35 °C (see Supplementary Material), yielded the Arrhenius parameters given in Table II.

Indirect Estimate of k^{SnH} for $Me_3SiCH_2CH_2^{\bullet}$ (2•). The trisubstituted arsine reacted with photochemically generated *tert*-butoxyls to yield the expected radical, 2•: EPR spectrum, $a^{H_\alpha}(2H) = 20.75$ G, $a^{H_\beta}(2H) = 19.0$ G, at 25 °C; lit.[19] $a^{H_\alpha}(2H) = 21.05$ G, $a^{H_\beta}(2H) = 17.68$ G at −112 °C. Unfortunately, this arsine, even after preparative GC, gave transients in the laser flash system.[15] For this reason, it was not possible to measure the rate constant for reaction of 2• with n-Bu_3SnH.[20] Radical 2• was also produced by photolysis of 3-(trimethylsilyl)propionyl peroxide and was identified by EPR spectroscopy. Unfortunately, this peroxide

$$(Me_3SiCH_2CH_2CO_2)_2 \xrightarrow{h\nu} \underset{\mathbf{2}^{\bullet}}{2Me_3SiCH_2CH_2^{\bullet}} + 2CO_2 \tag{7}$$

(which is relatively unstable at room temperature) was instantly decomposed by n-Bu_3SnH so that the laser flash experiments could not be performed.

Since our attempts to measure $k^{\text{SnH}}(\mathbf{2}^{\bullet})$ directly were unsuccessful, we were forced to consider indirect methods for estimating this quantity. Early kinetic studies on the free-radical chain reaction of alkyl bromides with n-Bu_3SnH showed that the rate-controlling propagation step was H-atom abstraction from the tin hydride by the alkyl radical.[22,23] The overall process can be represented by[22]

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(14) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 6161–6164.

(15) By the addition of benzhydrol as a "probe"[16] it is possible to measure rate constants for reaction of *tert*-butoxyl radicals with trialkylarsines. For $(Me_3SiCH_2)_3As$ this reaction has a rate constant $k_2 = (9.25 \pm 0.55) \times 10^8$ $M^{-1}\ s^{-1}$, for $(Me_3SiCH_2CH_2)_3As$ $k = (1.23 \pm 0.10) \times 10^9$ $M^{-1}\ s^{-1}$, while for $(MeCH_2)_3As$ we have previously shown[12] that $k = 2.5 \times 10^9$ $M^{-1}\ s^{-1}$. (A value for $(Me_3SiCH_2CH_2CH_2)_3As$ could not be obtained because transients were produced even in the absence of benzhydrol.) Note that the β-scission of trialkyl-*tert*-butoxyarsoranyl radicals, $R_3\dot{A}sOCMe_3$, is known[12] to be "instantaneous" on the time scale of these experiments, particularly in comparison with the rate of alkyl radical attack on tin hydride (reaction 4).

(16) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

(17) Compare[18] *n*-butyl, $a^{H_\alpha}(2H) = 21.98$ G, $a^{H_\beta}(2H) = 29.54$ G at −105 °C, with $\partial a^{H_\beta}/\partial T = -0.022$ G/K, which yields $a^{H_\beta}(2H) = 26.68$ G at 25 °C. It should be noted that $\partial a^{H_\beta}/\partial T$ is negative, not positive as given in ref 18.

(18) Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 7695–7701.

(19) Kawamura, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 648–650. Note: for $Me_3SiCH_2CH_2^{\bullet}$, $\partial a^{H_\beta}/\partial T$ is given as +0.013 G/K, from which we calculate that $a^{H_\beta}(2H) = 19.46$ G at 25 °C.

(20) (a) The remote possibility of a rapid β-scission, $\mathbf{2}^{\bullet} \rightarrow Me_3Si^{\bullet} + C_2H_4$ at these temperatures,[20b] was explored by laser flash photolysis of di-*tert*-butyl peroxide, $(Me_3SiCH_2CH_2)_3As$, and benzil (which is an excellent silyl radical trap).[21] No absorption was produced at 378 nm (the $\lambda_{\max}$ for the silyl radical/benzil adduct),[21] which allows us to eliminate this reaction from consideration under our conditions. (b) See: Bennett, S. W.; Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Organomet. Chem.* **1986**, *15*, P17. Jackson, R. A. *J. Chem. Soc., Chem. Commun.* **1974**, 573–574.

(21) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5119–5123.

(22) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047–7055.

(23) The rate-controlling step for alkyl chlorides is chlorine atom abstraction by the tri-*n*-butyltin radical.[22]

initiation

$$\mathrm{In_2} \xrightarrow{k_8} (2e)\mathrm{In}^\bullet \rightarrow \rightarrow (2ef)\mathrm{R}^\bullet \qquad (\text{rate} = R_i) \qquad (8)$$

propagation

$$\mathrm{R}^\bullet + n\text{-}\mathrm{Bu_3SnH} \xrightarrow{k^{\mathrm{SnH}}} \mathrm{RH} + n\text{-}\mathrm{Bu_3Sn}^\bullet \qquad (9)$$

$$n\text{-}\mathrm{Bu_3Sn}^\bullet + \mathrm{RBr} \xrightarrow{k_{\mathrm{RBr}}^{\mathrm{Sn}^\bullet}} n\text{-}\mathrm{Bu_3SnBr} + \mathrm{R}^\bullet \qquad (10)$$

termination

$$\mathrm{R}^\bullet + \mathrm{R}^\bullet \rightarrow \text{nonradical products} \qquad (11)$$

where $\mathrm{In_2}$ represents a thermal source of radicals, $\mathrm{In}^\bullet$, which yields these radicals with an efficiency e, and these radicals then initiate the chain with an efficiency f so as to produce a rate of chain initiation $R_i = 2efk_8[\mathrm{In_2}]$. The overall velocity of the reaction, V, is given by[22]

$$V = k^{\mathrm{SnH}}[n\text{-}\mathrm{Bu_3SnH}]R_i^{1/2}/(2k_{11})^{1/2} \qquad (\mathrm{I})$$

It is now firmly established[22,24-27] that small, sterically uncrowded, alkyl radicals undergo their bimolecular self-reactions with rates that are equal (or very close) to the diffusion-controlled limit. This means that for unhindered alkyl radicals of generally similar size and under similar experimental conditions, the values of $2k_{11}$ are effectively identical. Therefore, individual measurement of the overall rates of reaction, V_a and V_b, for two alkyl bromides, $\mathrm{R_aBr}$ and $\mathrm{R_bBr}$, with n-$\mathrm{Bu_3SnH}$ under conditions where the rate of chain initiation is equal and constant can be described by

$$V_a = k_a^{\mathrm{SnH}}[n\text{-}\mathrm{Bu_3SnH}]R_i^{1/2}/(2k_{11})^{1/2} \qquad (\mathrm{II})$$

$$V_b = k_b^{\mathrm{SnH}}[n\text{-}\mathrm{Bu_3SnH}]R_i^{1/2}/(2k_{11})^{1/2} \qquad (\mathrm{III})$$

For equal R_i and equal [n-$\mathrm{Bu_3SnH}$] we have

$$\frac{V_a}{V_b} = \frac{k_a^{\mathrm{SnH}}}{k_b^{\mathrm{SnH}}} \qquad (\mathrm{IV})$$

Provided k_a^{SnH} is known, k_b^{SnH} can be determined with acceptable precision.

Constant rates of chain initiation were achieved by the use of 2,2′-azobis(2,4-dimethylvaleronitrile) (DMVN) as the thermal source of initiating radicals. The progress of the reaction was monitored continuously by ^{1}H NMR by carrying out the reactions in degassed, sealed NMR tubes directly in the spectrometer's probe at 33 °C using $\mathrm{C_6D_6}$ as solvent. Unfortunately, the reaction of $\mathrm{Me_3SiCH_2Br}$ and of $\mathrm{Me_3SiCH_2CH_2Br}$ with n-$\mathrm{Bu_3SnH}$ were both somewhat too rapid for convenient and accurate measurement of their rates by NMR. For this reason, n-$\mathrm{Bu_3GeH}$ was used in place of n-$\mathrm{Bu_3SnH}$. The two radicals n-$\mathrm{Bu_3Ge}^\bullet$ and n-$\mathrm{Bu_3Sn}^\bullet$ are known to abstract bromine from alkyl bromides with very similar rate constants.[28] However, n-$\mathrm{Bu_3GeH}$ is at least an order of magnitude less active than n-$\mathrm{Bu_3SnH}$ as a hydrogen atom donor to alkyl radicals.[29,30] As a consequence, the rate of the overall chain reaction is reduced and the kinetic rate law (eq I) that is known[22] to describe the alkyl bromide/tin hydride reaction will be strongly reinforced for the alkyl bromide/germanium hydride reaction, i.e., eq V.

Table III. Kinetic Data Obtained by ^{1}H NMR for the DMVN-Initiated Reaction of n-$\mathrm{Bu_3GeH}$ with Four Bromides in $\mathrm{C_6D_6}$ at 33 °C

[bromide],[a] M	[n-$\mathrm{Bu_3GeH}$],[a] M	[DMVN],[a] M	10^5V,[b] M s^{-1}	10^5V,[c] M s^{-1}	10^5V/[n-$\mathrm{Bu_3GeH}$]-[DMVN]$^{1/2}$,[d] M$^{-1/2}$ s^{-1}
		$\mathrm{Me_3SiCH_2Br}$			
1.00	0.10	0.15	0.69	0.85	20
1.00	0.33	0.15	4.1	5.4	37
1.00	0.50	0.10	6.3	7.2	43
1.00	0.50	0.50	16.8		48
1.00	0.50	1.00	19.4		39
1.00	0.65	0.15	12.3	12.4	49
1.00	0.97	0.15	17.0	12.7	40
3.00	0.50	0.15	8.8		45
		$\mathrm{Me_3SiCH_2CH_2Br}$			
1.16	0.11	0.15	0.22		5.2
1.16	0.32	0.15	0.60	0.60	4.8
1.00	0.50	0.10	1.1	1.0	6.6
1.00	0.50	0.50	1.9	2.4	6.1
1.00	0.50	1.00	2.4	2.4	4.8
1.16	0.65	0.15	1.4	1.1	5.0
1.16	0.97	0.15	2.4	1.8	5.6
3.00	0.50	0.15	1.1		5.7
		$\mathrm{Me_3SiCH_2CH_2CH_2Br}$			
1.04	0.10	0.15	0.29	0.22	6.6
1.04	0.32	0.15	0.61	0.77	5.6
1.00	0.50	0.15	1.3	1.2	6.5
1.00	0.50	0.25	1.7	1.2	5.8
1.00	0.50	0.98	3.5		7.1
1.04	0.64	0.15	1.5	1.4	5.8
1.04	0.94	0.15	2.9	2.1	6.9
3.00	0.50	0.15	1.2		6.2
		$\mathrm{CH_3CH_2CH_2CH_2Br}$			
1.00	0.10	0.15	0.29		7.5
1.00	0.25	0.15	0.69	0.60	6.7
1.00	0.50	0.15	1.4	1.5	7.5
1.00	0.50	0.25	1.7	2.1	7.6
1.00	0.50	0.50	3.0	3.5	9.2
1.00	0.50	0.75	2.8	3.3	7.0
3.00	0.50	0.15	1.4		7.2

[a] Initial concentration. [b] Monitored via the Ge*H* signal. [c] Monitored via the C*H*$_2$Br signal. [d] The averaged value of V has been used in those cases where V was measured via both the Ge*H* and C*H*$_2$Br signals.

$$\mathrm{R}^\bullet + n\text{-}\mathrm{Bu_3GeH} \xrightarrow{k^{\mathrm{GeH}}} \mathrm{RH} + n\text{-}\mathrm{Bu_3Ge}^\bullet \qquad (12)$$

$$n\text{-}\mathrm{Bu_3Ge}^\bullet + \mathrm{RBr} \xrightarrow{k_{\mathrm{RBr}}^{\mathrm{Ge}^\bullet}} n\text{-}\mathrm{Bu_3GeBr} + \mathrm{R}^\bullet \qquad (13)$$

$$V = k^{\mathrm{GeH}}[n\text{-}\mathrm{Bu_3GeH}]R_i^{1/2}/(2k_{11})^{1/2} \qquad (\mathrm{V})$$

Since the rate of chain initiation is proportional to the DMVN concentration, eq V can be rewritten as

$$\frac{V}{[n\text{-}\mathrm{Bu_3GeH}][\mathrm{DMVN}]^{1/2}} = \frac{ck^{\mathrm{GeH}}}{(2k_{11})^{1/2}} \qquad (\mathrm{VI})$$

The experimental rate data obtained for the DMVN-initiated reaction of n-$\mathrm{Bu_3GeH}$ with $\mathrm{Me_3SiCH_2Br}$, $\mathrm{Me_3SiCH_2CH_2Br}$, $\mathrm{Me_3SiCH_2CH_2CH_2Br}$, and $\mathrm{CH_3CH_2CH_2CH_2Br}$ at 33 °C are given in Table III. As can be seen from the final column for each bromide, the quantity $V/[n\text{-}\mathrm{Bu_3GeH}][\mathrm{DMVN}]^{1/2}$ is constant within our experimental error and, in particular, shows no dependence on the bromide concentration (within the range 1–3 M).

Measurement of the Relative Rates of Bromine Atom Abstraction from Silicon-Containing Bromides and *n*-Butyl Bromide. Relative values of the rate constants for reaction 13 ($k_{\mathrm{RBr}}^{\mathrm{Ge}^\bullet}$) were measured by standard competitive-kinetic methods at 33 °C using DMVN as the thermal initiator of the radical-chain processes. The reactivities of the three silicon-containing bromides (**1**-Br, **2**-Br, and **3**-Br) were each measured relative to n-butyl bromide by moni-

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(24) Watts, G. B.; Ingold, K. U. *J. Am. Chem. Soc.* **1972**, *94*, 491–494.

(25) Ingold, K. U. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 2.

(26) Griller, D.; Ingold, K. U. *Int. J. Chem. Kinet.* **1974**, *6*, 453–456.

(27) See also: Schuh, H.; Fisher, H. *Int. J. Chem. Kinet.* **1976**, *8*, 341–356; *Helv. Chim. Acta* **1978**, *61*, 2130–2164, 2463–2481. Lehni, M.; Schuh, H.; Fisher, H. *Int. J. Chem. Kinet.* **1979**, *11*, 705–713. Paul, H.; Segaud, C. *Ibid.* **1980**, *12*, 637–647. Huggenberger, C.; Fisher, H. *Helv. Chim. Acta* **1981**, *64*, 338–353. Münger, K.; Fisher, H. *Int. J. Chem. Kinet.* **1984**, *16*, 1213–1226. Lipscher, J.; Fisher, H. *J. Phys. Chem.* **1984**, *88*, 2555–2559 and references cited.

(28) Ingold, K. U.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 343–348.

(29) Lusztyk, J.; Maillard, B.; Lindsay, D. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 3578–3580.

(30) Lusztyk, J.; Maillard, B.; Deycard, S.; Lindsay, D. A.; Ingold, K. U. *J. Org. Chem.* **1987**, *52*, 3509–3514.

Table IV. Relative and Absolute Rate Constants for Some Bromine Atom Abstraction Reactions at Ambient Temperatures

	n-$Bu_3Ge^\bullet$		n-$Bu_3Sn^\bullet$	
halide	rel k^a	$10^{-7}k_{\mathrm{RBr}}^{\mathrm{Ge}^\bullet}$, $M^{-1}\ s^{-1}$	rel k^b	$10^{-7}k_{\mathrm{RBr}}^{\mathrm{Sn}^\bullet}$, $M^{-1}\ s^{-1}$
Me_3SiCH_2Br (**1**-Br)	3.3	15.2	6.6	21.1
$Me_3SiCH_2CH_2Br$ (**2**-Br)	1.7	7.8	3.7	11.8
$Me_3SiCH_2CH_2CH_2Br$ (**3**-Br)	0.71	3.3	1.1	3.4
$CH_3CH_2CH_2CH_2Br$	(1.0)	4.6[c]	(1.0)	3.2[d]

[a] This work. Errors are ca. ±20%. [b] Reference 31 at 35–40 °C. [c] From ref 28 at 29 °C. [d] From ref 28 at 25 °C.

Table V. Relative and Absolute Rate Constants for the Reactions of Some Carbon-Centered Radicals with n-Bu_3GeH at 33 °C and Rate Constant Ratios for Attack of These Radicals on n-Bu_3SnH to Attack on n-Bu_3GeH at the Same Temperature

radical	rel k^{GeH} [a]	$10^{-5}k^{\mathrm{GeH}}$, $M^{-1}\ s^{-1}$	$k^{\mathrm{SnH}}/k^{\mathrm{GeH}}$
$Me_3SiCH_2^\bullet$ (**1**$^\bullet$)	5.2 ± 1.3	6.3	$40._6$
$Me_3SiCH_2CH_2^\bullet$ (**2**$^\bullet$)	0.73 ± 0.09	0.88	
$Me_3SiCH_2CH_2CH_2^\bullet$ (**3**$^\bullet$)	0.83 ± 0.07	1.0	$24._3$
$CH_3^\bullet$		(~5)[c]	18[c]
$CH_3CH_2CH_2CH_2^\bullet$	(1.0)[b] ± 0.1	1.2_1[d]	$22._4$

[a] Calculated from data in Table III with a double weighting for runs in which V was measured by using the ^1H NMR signals from both Ge*H* and C*H*$_2$Br. The error limits correspond to one standard deviation. [b] Assumed. [c] At room temperature. This value is based on the absolute rate constant for the reaction of $CH_3^\bullet$ with n-Bu_3SnH[12] and a pair of competitive experiments involving the reaction of CH_3I with n-Bu_3SnH/n-Bu_3SnD and n-Bu_3SnD/n-Bu_3GeH as described in ref 33. These experiments showed that the tin hydride was 18 times as reactive toward $CH_3^\bullet$ as the germanium hydride. For a discussion of this experiment, see ref 29. [d] See ref 29 and text.

toring the loss of the two bromides (e.g., **1**-Br and n-BuBr) both by GC (except for **2**-Br, which was totally decomposed on the GC column) and by ^1H NMR (except for **3**-Br for which the C*H*$_2$Br signal was too close to the C*H*$_2$Br signal from n-BuBr). These measured rate constant ratios are given in Table IV. They have been converted to absolute rate constants by making use of the previously measured value of $k_{\mathrm{RBr}}^{\mathrm{Ge}^\bullet}$ for 1-bromopropane at 29 °C.[28] (It can be safely assumed that the variation in rate constant ratios over the 29–33 °C temperature range will be less than the error in the measurements.) Relative[31] and derived absolute rate data for bromine atom abstraction by tri-n-butyltin radicals (reactions 10) have also been given for comparative purposes in Table IV. These results serve to confirm our earlier conclusion[28] that n-$Bu_3Ge^\bullet$ and n-$Bu_3Sn^\bullet$ radicals abstract halogen atoms with very similar rate constants. Furthermore, it is clear that the rate of bromine atom abstraction from the silicon-containing bromides by n-$Bu_3Ge^\bullet$ (reaction 13) is very much faster than hydrogen atom abstraction by the derived carbon-centered radicals from n-Bu_3GeH (reaction 12) (vide infra). The kinetic conditions necessary for rate law V to obtain are therefore fulfilled.

Discussion

All four radicals listed in Table III obey the kinetic rate law described by eq VI. The average values of $V/[n\text{-}Bu_3GeH][DMVN]^{1/2}$, which is equal to $ck^{\mathrm{GeH}}/(2k_{11})^{1/2}$, for each radical (see Table V) can be used to derive relative k^{GeH} values since c (which depends on the rate of thermal decomposition of DMVN and the overall efficiency, *ef*, with which the radicals generated initiate the chain reaction) must be identical in each system and since the values of $2k_{11}$ must be very similar for each radical.[22,24–27] Furthermore, these relative k^{GeH} values can be converted to absolute rate constants if we make the reasonable assumption that k^{GeH} for the n-butyl radical is the same as k^{GeH} for the 5-hexenyl radical.[32] The latter rate constant has been determined over a range of temperatures by making use of the 5-hexenyl radical's cyclization to "clock" its rate of hydrogen abstraction from tri-n-butylgermanium hydride.[29] At 33 °C this rate constant has a value of $1.2_1 \times 10^5\ M^{-1}\ s^{-1}$.

Either the relative or the derived "absolute" k^{GeH} values listed in Table V clearly demonstrate that there is a "silicon effect" on hydrogen abstraction from germanium hydride, just as there is for hydrogen abstraction from the tin hydride (see Table II). Although the germane data were obtained at only one temperature, it will be considered first since results are available for silicon situated α (radical **1**$^\bullet$), β (**2**$^\bullet$), and γ (**3**$^\bullet$) to the radical center.

The α-substituted radical is appreciably more reactive than n-butyl and even appears to be slightly more reactive than the methyl radical. We attribute this reactivity to the ability of the silicon to stabilize developing negative charge in the transition state—the "α-effect", which is well-known in heterolytic organosilicon chemistry,[34] and which has been invoked previously to rationalize other reactions of α-substituted silyl radicals.[31,35] The

$$Me_3SiCH_2^\bullet + HMBu_3 \rightarrow [Me_3Si\overset{\delta-}{C}H_2\text{---}H\text{---}\overset{\delta+}{M}Bu_3]^{\bullet\ddagger} \rightarrow Me_4Si + \dot{M}Bu_3 \qquad (M = Ge, Sn) \quad (14)$$

C–H bond in Me_4Si is generally believed to be weaker than primary C–H bonds in alkanes,[36–39] perhaps by as much as 2.6 kcal/mol,[39] so the reaction of **1**$^\bullet$ with the germane should be less exothermic than the corresponding reaction of the n-butyl radical. It is clear that any rate-retarding effect due to the reduced exothermicity is more than outweighed by the rate-accelerating effect due to polar contributions stabilizing the transition state for reaction 14.

The β-silyl-substituted radical, **2**$^\bullet$, is slightly less reactive toward the germane than is the n-butyl radical. The difference is small but significant and can be attributed to the mutual reinforcing action of two factors. First, the stabilization by silicon of neighboring negative charge (cf. eq 14) would tend to destabilize the transition state for the reaction of **2**$^\bullet$ with the germane since it would favor the development of positive charge at the radical center[40] and this would inhibit stabilization of the transition state by charge dispersal in the direction shown in reaction 14. Second, primary C–H bonds that are β to a silicon atom are also appreciably weaker than primary C–H bonds in alkanes,[38,39,41] again perhaps by as much as 2.6–3.0 kcal/mol.[39,41] Thus, both polar and thermochemical effects would be expected to make **2**$^\bullet$ less reactive that the n-butyl radical. Indeed, when compared with the 5.5-fold increase in reactivity of a primary hydrogen in Et_4Si

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(31) Wilt, J. W.; Belmonte, F. G.; Zieske, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 5665–5675.

(32) This procedure was employed because of the difficulties involved in determining R_i by the induction period method in these types of reaction mixtures.[33] The overall efficiency of chain initiation, *ef*, by DMVN in these systems is very low, as has been remarked upon previously for the related initiator 2,2′-azobis(isobutyronitrile).[33] Thus, for DMVN at 33 °C, $k_8 = 1.45 \times 10^{-6}\ s^{-1}$; if we take[22,24–27] $2k_{11}$ to be $10^{10}\ M^{-1}\ s^{-1}$ (a maximum value) and k^{SnH} for n-butyl radical to be $1.2 \times 10^5\ s^{-1}$ at 33 °C,[29] then, from the mean value of $V/[n\text{-}Bu_3GeH][DMVN]^{1/2}$ for n-butyl bromide of $7.5_6 \times 10^{-5}\ M^{-1/2}\ s^{-1}$, we calculate that *ef* ~0.001. Such an extremely low efficiency may be partly due to the fact that the initiating radical, which is both tertiary[30] and stabilized by the neighboring cyano group, will not attack the germanium hydride very readily. However, a few trial experiments with n-Bu_3GeH, n-BuBr, and di-*tert*-butyl hyponitrite, a thermal initiator that yields the highly reactive *tert*-butoxyl radical, gave, from the measured reaction rates, an *ef* value of only ~0.006. We are at a loss to explain these results.

(33) Carlsson, D. J.; Ingold, K. U.; Bray, L. C. *Int. J. Chem. Kinet.* **1969**, *1*, 315–323.

(34) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981; pp 21–29. For recent work, see, e.g.: Prezzavento, B. A.; Kuivila, H. G. *J. Org. Chem.* **1987**, *52*, 929–931 and references cited.

(35) Wilt, J. W.; Aznavoorian, P. M. *J. Org. Chem.* **1978**, *43*, 1285–1286.

(36) Doncaster, A. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2908–2916. See also: Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246–252.

(37) Wilt, J. W.; Kolewe, O.; Kraemer, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 2624–2631.

(38) Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. *J. Am. Chem. Soc.* **1985**, *107*, 208–211.

(39) Davidson, I. M. T.; Barton, T. J.; Hughes, K. J.; Ijadi-Maghsoodi, S.; Revis, A.; Paul, G. C. *Organometallics* **1987**, *6*, 644–646.

(40) This, the "β-effect", is also a well-known phenomenon in ionic organosilicon chemistry; see ref 34, pp 15–20. For a recent successful application of the β-effect to a synthetic problem, see: Magnus, P.; Cairns, P. M.; Moursounidis, J. *J. Am. Chem. Soc.* **1987**, *109*, 2469–2471.

(41) Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207–208.

toward abstraction by *tert*-butoxyl relative to abstraction of a primary hydrogen from *n*-pentane[38] or with the 3.7-fold increase in reactivity for chlorine abstraction, or the 6.6-fold increase in reactivity for bromine abstraction, from $\mathrm{Me_3SiCH_2CH_2X}$ by $n\text{-}\mathrm{Bu_3Sn}^\bullet$ relative to abstraction from the corresponding 1-halopentanes,[31] what is surprising is that $\mathbf{2}^\bullet$ is only ca. 27% less reactive than the *n*-butyl radical toward $n\text{-}\mathrm{Bu_3GeH}$. Ethylene is known to be an excellent trap for silicon-centered radicals.[42,43] Our inability to detect the β-scission reaction[20a]

$$\mathrm{Me_3SiCH_2CH_2^\bullet \rightarrow Me_3Si^\bullet + C_2H_4} \qquad (15)$$

was therefore expected.[20b,42]

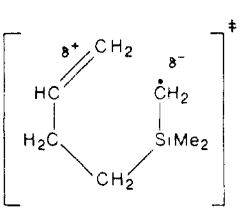
The γ-silyl-substituted radical, $\mathbf{3}^\bullet$, has a reactivity lying between that of $\mathbf{2}^\bullet$ and *n*-butyl. The remoteness of the silicon atom from the radical center would be expected to attenuate any deactivating polar[45] or thermochemical effects almost to insignificance. We therefore assign the slightly lower reactivity of $\mathbf{3}^\bullet$ (relative to *n*-butyl) to minor steric effects associated with the bulky trimethylsilyl group.[47]

The foregoing remarks regarding the reactivities of $\mathbf{1}^\bullet$, $\mathbf{3}^\bullet$, and the *n*-butyl radical toward $n\text{-}\mathrm{Bu_3GeH}$ (see Table V) also apply to their reactivities toward $n\text{-}\mathrm{Bu_3SnH}$ (see Table II). Indeed, at ambient temperatures even their relative reactivities toward the two hydrides are rather similar; viz., $\mathbf{1}^\bullet/n$-butyl = 5.2($n\text{-}\mathrm{Bu_3GeH}$) and 9.3($n\text{-}\mathrm{Bu_3SnH}$); $\mathbf{3}^\bullet/n$-butyl = 0.83($n\text{-}\mathrm{Bu_3GeH}$) and 0.92($n\text{-}\mathrm{Bu_3SnH}$).

The Arrhenius parameters for the $\mathbf{3}^\bullet$/tin hydride reaction are subject to rather large error limits (see Table II). Since the reactivities of $\mathbf{3}^\bullet$ and *n*-butyl toward $n\text{-}\mathrm{Bu_3SnH}$ at 300 K are rather similar, we suggest that the true Arrhenius parameters for the $\mathbf{3}^\bullet$/tin hydride reaction are probably similar to those for the *n*-butyl radical. The enhanced reactivity of $\mathbf{1}^\bullet$ toward $n\text{-}\mathrm{Bu_3SnH}$ would, however, appear to be mainly or even entirely due to an elevated Arrhenius preexponential factor. In atom abstractions, as we have first pointed out,[49] a strong polar contribution to the transition state (eq 14) manifests itself principally as an enhaced A factor because it promotes a "looser" transition state.[50-52]

The rate constant ratios for radical attack on tin hydride or germanium hydride at 33 °C, viz., $k^{\mathrm{SnH}}/k^{\mathrm{GeH}}$, that are listed in Table V range from ca. 18 to 41. The higher reactivity of the tin hydride reflects primarily[52] the fact that the Sn–H bond is some 8–10 kcal/mol weaker than the Ge–H bond.[33,53] With the exception of $\mathbf{1}^\bullet$ (for which special arguments can be advanced[52]), these rate constant ratios lie in the range of ca. 18–24. We can see no reason why a similar ratio, say 22, should not apply to the β-silicon-substituted radical, $\mathbf{2}^\bullet$. With this assumption,[54] we are now in a position to achieve our primary objective, namely, the conversion of the data[8] on cyclization vs hydrogen abstraction from $n\text{-}\mathrm{Bu_3SnH}$ for the three silicon-containing analogues of the 5-hexenyl radical that have been summarized in Table I into absolute rate constants for the various cyclization process. The results of these calculations are given in Table VI.

The calculated rate constants for the endo cyclization of the three silicon-containing radicals to form dimethylsilacyclohexyl radicals are not greatly different from the rate constants for the endo cyclization of the parent 5-hexenyl radical (nor, probably, from the rate constant for endo cyclization of 2,2-dimethyl-5-hexenyl; see footnote *f* in Table VI). The fastest of the endo cyclizations involves the α-silicon-substituted radical and probably reflects two factors. First, there will be a rate-accelerating effect arising from an easier approach to the $\mathrm{CH_2}$ end of the double bond since C–Si bonds are ca. 25% longer than C–C bonds.[55] Second, although polar contributions to the transition state for 5-hexenyl type exo cyclization are generally considered to involve the development of fractional positive charge at the radical center and fractional negative charge in the double bond,[7a,c,56] we see no reason why charge separation in the opposite sense, which would be favored by the α-silicon (vide supra), i.e.,



should not also stabilize the transition state and hence accelerate endo cyclization.

There is a much wider variation in the magnitudes of the exo cyclization rate constants than for the endo cyclizations. First, it is clear that the rate-accelerating, *gem*-dimethyl (Thorpe–Ingold)[57] effect[58,59] which is so obvious in *gem*-dimethyl-substituted, all-carbon 5-hexenyl exo cyclizations[7a,c,60-62] (cf. also 2,2-dimethyl-5-hexenyl vs 5-hexenyl (Table VI)) is not apparent in the dimethylsilyl-substituted 5-hexenyl radicals. This is not entirely surprising since the generally accepted explanation[59] of this effect is that the two methyl substituents produce extra gauche interactions in the ground state which are partly relieved when the cyclic transition state is obtained so that the rate of ring closure is enhanced. The longer Si–C bond will make such factors much less important in the dimethylsilyl-substituted radicals.

Second, the relatively low rate constants for exo cyclization of the α- and γ-dimethylsilyl-substituted radicals can probably be attributed to bond-length effects which make it difficult for the radical center to approach the CCH end of the double bond. However, the failure to detect any exo-cyclized product from the

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[42] Davies, A. G.; Griller, D.; Roberts, B. P. *J. Organomet. Chem.* **1972**, *38*, C8–C10.

[43] Note that the corresponding carbocation fragments readily, which eases the ionic cleavage of bromides such as **2**-Br.[44]

[44] Sommer, L. H.; Bailey, D. L.; Goldberg, G. M.; Buck, C. E.; Bye, T. S.; Evans, F. J.; Whitmore, F. C. *J. Am. Chem. Soc.* **1954**, *76*, 1613–1618.

[45] Note that γ-silicon has been shown to stabilize developing positive charge in a solvolytic reaction,[46] a polar effect that would be deactivating in the present reaction.

[46] Shiner, V. J., Jr.; Ensinger, M. W.; Rutkowske, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 804–809.

[47] Molecular models show that in certain conformations of $\mathbf{3}^\bullet$ there will be steric hindrance to the approach of the metal hydride. This kind of steric problem involves the classic "rule of six" that was demonstrated many years ago.[48] Radical $\mathbf{3}^\bullet$ has a "six number" of 9,[48] which is relatively high.

[48] Neumann, M. S. *J. Am. Chem. Soc.* **1950**, *72*, 4783–4786.

[49] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123–5127.

[50] For a second example of this phenomenon, see: Chatgilialoglu, C. *J. Org. Chem.* **1986**, *51*, 2871–2873.

[51] For an interesting, new approach to those atom abstractions in which electron transfer is a significant component in the reaction process, see: Lee, K.-W.; Brown, T. L. *J. Am. Chem. Soc.* **1987**, *109*, 3269–3275.

[52] A significant polar contribution to the transition state for the reaction of $\mathbf{1}^\bullet$ with $n\text{-}\mathrm{Bu_3SnH}$ is also suggested by the fact that $k^{\mathrm{SnH}}/k^{\mathrm{GeH}}$ (see Table IV) is about twice as large for $\mathbf{1}^\bullet$ as it is for $\mathbf{3}^\bullet$, $\mathrm{CH_3}^\bullet$, and *n*-butyl, a phenomenon we attribute to the greater ability of tin to accept positive charge when compared with germanium; i.e., the polar effect shown in eq 14 is more pronounced with the tin hydride.

[53] Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17–19.

[54] That is, k^{SnH} for $\mathbf{2}^\bullet$ and for the analogous β-silicon-substituted 5-hexenyl radical has a value = $22 \times 0.72_5 \times k^{\mathrm{GeH}}$ for the *n*-butyl radical at ambient temperatures. Taking $k^{\mathrm{GeH}}(n\text{-butyl}) = 9.8 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ at 25 °C[29] (see text also) yields $k^{\mathrm{SnH}}(\mathbf{2}^\bullet) = 1.5_6 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$ at this temperature.

[55] We have previously used this bond-length argument to help explain the very rapid and exclusively endo cyclization of pent-4-enylsilyl radicals[9a] such as $\mathrm{CH_2{=}CHCMe_2CH_2CH_2SiMe_2}$.

[56] The incoming radical behaves as a nucleophile, with the dominant interaction involving the semioccupied $2p_z$ orbital and one lobe of the vacant π^* orbital.

[57] Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, *107*, 1080–1106. Ingold, C. K. *Ibid.* **1921**, *119*, 305–329.

[58] Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962; pp 196–202. Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Interscience: New York, 1965; pp 191–192.

[59] Allinger, N. L.; Zalkow, V. *J. Org. Chem.* **1960**, *25*, 701–704. Gream, G. E.; Serelis, A. K. *Aust. J. Chem.* **1978**, *31*, 863–891 and references cited.

[60] Beckwith, A. L. J.; Lawrence, T. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1535–1539.

[61] Beckwith, A. L. J.; Easton, C. J.; Lawrence, T.; Serelis, A. K. *Aust. J. Chem.* **1983**, *36*, 545–556.

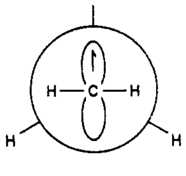
[62] Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron Lett.* **1985**, *26*, 373–376.

Table VI. Rate Constants for the Cyclization of 5-Hexenyl and Some Substituted 5-Hexenyl Radicals at 25 °C

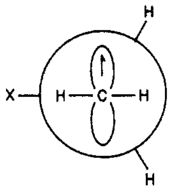
radical	$10^{-6}k^{SnH}$,[a] $M^{-1}\ s^{-1}$	$10^{-4}k_c^{5+6}$,[b] s^{-1}	$10^{-4}k_{exo}^{5}$, s^{-1}	$10^{-4}k_{endo}^{6}$, s^{-1}
$CH_2{=}CHCH_2CH_2SiMe_2CH_2^{\bullet}$	21.5[c]	2.3_7	0.7_5	1.6_2
$CH_2{=}CHCH_2SiMe_2CH_2CH_2^{\bullet}$	1.5_6[d]	0.10_4	~0	0.10
$CH_2{=}CHSiMe_2CH_2CH_2CH_2^{\bullet}$	2.0_5[c]	6.7_7	6.3_5	0.4_2
$CH_2{=}CHCH_2CH_2CH_2CH_2^{\bullet}$	2.3_1[c]	$24._5$	$24._2$	0.3_4
$CH_2{=}CHCH_2CH_2CMe_2CH_2^{\bullet}$	3.3_1[e]	>200	>200	f

[a] At 25 °C. [b] $k_c^{5+6} = k_{exo}^{5} + k_{endo}^{6}$. [c] From Table II. [d] See footnote 54 and text. [e] Calculated from Arrhenius parameters given in ref 13 for the neopentyl radical. [f] Small, but could be ca. 0.2 (i.e., ca. 2 × $10^3\ s^{-1}$) based on yield limits given in ref 8.

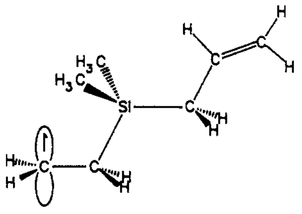
β-silicon-substituted radical[8] implies that there must be one (or more) additional factor(s) which hinder exo cyclization in this case. Certainly this factor cannot simply be some steric destabilization of the transition state since the all-carbon analogue, $CH_2{=}CHCH_2CMe_2CH_2CH_2^{\bullet}$, undergoes exo cyclization some 20-times faster than 5-hexenyl at ambient temperatures.[61,63] Following an earlier speculation[8] we suggest that the difficulty experienced by the β-silicon-substituted radical in undergoing exo cyclization is associated with the perpendicular conformation, P, which is preferred relative to the eclipsed conformation, **E**, by β-substituted ethyl radicals containing a second-row element as the substituent.[19,64-66] The rather strong preference of β-silylethyl radicals for conformation P (a preference that is worth ca. 1.3 kcal/mol)[67] may be accompanied by a preference of the $H_2C{=}CHCH_2SiMe_2CH_2CH_2^{\bullet}$ radical for a ground-state conformation, A. Distortion to the transition-state conformation, **B**, would be substantially disfavored if there is also an appreciable barrier to rotation about the C_β–Si bond and/or the Si_γ–C_δ bond in such radicals.



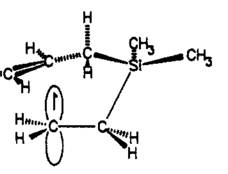
P



E



A



B

Experimental Section

General. Melting points were taken on a calibrated Fisher-Johns block or a Fisher Model 355 digital melting point analyzer. The following instruments were used to determine spectra: **UV**, Cary Model 219 (values are given in nm); **IR**, Perkin-Elmer Model 700 or 1330 instruments, Beckman Acculab (neat samples were run as thin films, solutions in chloroform were run in matched cells, values are given in cm^{-1}); **NMR**, Varian EM-360A (the usual abbreviations for signals are used with the ranges of multiplets given unless they were clearly first order with observable *J* values; the spectra normally were referenced to TMS or, in its absence, to benzene or $CHCl_3$ (δ 7.23) (values are given in ppm)); **ESR**, Varian E-line Model E-104A. **GC** work was performed on a Varian Aerograph 920 with helium as the carrier gas at 160 mL/min. **GC/MS** determinations were carried out on a Hewlett-Packard Model 5995. The laser flash photolysis apparatus has been described in earlier papers.[12,13,16,21,28,49] Microanalyses were performed by Micro-Tech Laboratories, Skokie, IL.

Materials. Tri-*n*-butyltin hydride was commercial material (Aldrich) or was prepared as reported.[68]

Tri-*n*-butylgermanium hydride was made by reduction of tri-*n*-butylgermanium bromide with $LiAlH_4$ in benzene containing benzyltriethylammonium chloride:[69] 87%; distilled in a Hickman still at 0.1 mm, 80 °C (lit.[70] bp 61–63 °C at 0.3 mm); IR (neat) 2000 (GeH); ^1H NMR ($CDCl_3$, TMS) 3.67 (septet, *J* = ca. 3 Hz, GeH). The above bromide[71] and its precursor, tetra-*n*-butylgermane,[72] were each obtained as described.

Tris[(trimethylsilyl)methyl]arsine was synthesized as reported:[73] 66%, mp 67–68.5 °C (lit.[73] mp 67–68.5 °C); ^1H NMR ($CDCl_3$, no TMS) 0.66 (s, CH_2), 0.05 (s, Me); mercurichloride derivative mp 169–170 °C (lit.[73] mp 176–176.8 °C).

Tris[β-(trimethylsilyl)ethyl]arsine was prepared from **β-(trimethylsilyl)ethyl bromide.** The latter compound was obtained as reported[44] by homolytic addition of HBr to the vinylsilane: 87%; unstable oil, purified by chromatography on silica gel (an intense orange band develops due to impurity). **Caution**: never dry the bromide over Na_2SO_4; a rapid decomposition can set in liberating gases.[74] Use immediately or store for short periods in a freezer. IR (neat) 1250, 825 (broad) (Me_3Si); ^1H NMR ($CDCl_3$, no TMS) 3.69–3.33 (cmplx m, CH_2Br), 1.50–1.10 (cmplx m, $SiCH_2$), 0.0 (s, SiMe). Conversion of the bromide to the Grignard reagent was performed as described.[75] This ethereal Grignard reagent (400 mL containing 142 mmol of reagent by titration) was treated dropwise with $AsCl_3$ (6.44 g, 35.5 mmol) in additional dry ether (150 mL) under nitrogen at 25 °C with stirring. The reaction was then continued under reflux for 4 days, during which time salts (whitish becoming chocolate) precipitated. All subsequent operations were done in a glovebag under nitrogen. The chilled solution was treated with NH_4Cl solution (saturated, 100 mL), HCl (10%, 200 mL), and water (100 mL). The phases were separated and the ether phase was washed with $NaHCO_3$ (5%, 200 mL) and brine (200 mL). If the ether phase was dark at this point, decolorizing carbon/Celite was used and the material was filtered. After being dried (Na_2SO_4), the solution was freed of solvent by rotary evaporation. The residual oil was distilled in a Kugelrohr apparatus. At 0.4 mm and 45 °C the coupled product, **1,4-bis(trimethylsilyl)butane,** collected (42%; IR (neat) 1250, 850 (Me_3Si); ^1H NMR ($CDCl_3$, no TMS) 1.50–1.17 (cmpx m, 2,3-CH_2's), 0.67–0.33 (cmplx m, 1,4-CH_2's), 0.0 (s, SiMe)) followed at 0.1 mm and 70–90 °C by crude tris[β-(trimethylsilyl)ethyl]arsine: colorless oil, 30%; IR (neat) 1250, 850 (Me_3Si); ^1H NMR ($CDCl_3$, no TMS) 1.55–1.07 (cmplx m, CH_2As), 0.72–0.37 (cmplx m, $SiCH_2$), 0.0 (s, SiMe); MS (*m/e*), P calcd 378.16; found 378.00. Attempts to make a mercurichloride or methiodide derivative failed. The pot residue eventually solidified. Recrystallization of this material from ether gave **bis[β-(trimethylsilyl)ethyl]chloroarsine**: ca. 20%; mp 166–168 °C; positive $AgNO_3$ test. Anal. Calcd for $C_{10}H_{26}AsClSi_2$: C, 38.39; H, 8.38. Found: C, 38.90; H, 8.26. This chloroarsine was immediately reduced with *n*-Bu_3SnH. The $(Me_3SiCH_2CH_2)_3As$ oxidized in air, particularly quickly as a thin film or upon exposure to air during TLC, but preparative GC (5% OV-101 column at 200 °C) gave material of apparently high purity: MS (*m/e*), P + 1, P + 2, and P + 3 % calcd: 32.16, 14.85, and 3.16, respectively. Found: 31.3, 15.2, and 3.0. This oil was stored under nitrogen and used in the laser flash photolysis study.

β-(Trimethylsilyl)propionyl peroxide was obtained as reported:[76] 76%, mp 28.7–29.7 °C (lit.[76] mp 30 °C); IR (CCl_4) 1820, 1788 (CO); ^1H NMR (CCl_4, PhH standard) 2.53–2.16 (cmplx m, CH_2CO), 1.40–0.80

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(63) For $CH_2{=}CHCH_2CMe_2CH_2CH_2^{\bullet}$ at 25 °C, $k_{exo}^{5} = 5.2 \times 10^6\ s^{-1}$ and $k_{endo}^{6} < 1 \times 10^5\ s^{-1}$; the Arrhenius parameters for the exo cyclization are log (A/s^{-1}) = 10.5 and *E* = 5.1 kcal/mol.[61]

(64) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 6161–6164; **1971**, *93*, 846–860.

(65) Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6715–6720. Symons, M. C. R. *Tetrahedron Lett.* **1975**, 793–796. See also: Stock, L. M.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1975**, *97*, 5620–5622.

(66) (a) Fossey, J. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merényi, R., Eds.; Reidel: Dordrecht, 1986; pp 87–90. (b) Bernardi, F.; Bottoni, A.; Fossey, J.; Sorba, J. *Tetrahedron* **1986**, *42*, 5567–5580.

(67) The barrier to rotation about the C_α–$C^{\bullet}$ bond has been estimated from the temperature dependence of H_β EPR hyperfine splittings to be 1.2 kcal/mol for $Et_3SiCH_2CH_2^{\bullet}$ (conformation P preferred) but only 0.4 kcal/mol for $CH_3CH_2CH_2^{\bullet}$ (conformation E preferred).[19] Ab initio calculations[66] have yielded $\Delta E = E(E) - E(P) = +1.36$ and +0.09 kcal/mol for $SiH_3CH_2CH_2^{\bullet}$ and $CH_3CH_2CH_2^{\bullet}$, respectively.

(68) Kuivila, H. G.; Beumel, O. F., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 1246–1250.

(69) Gevorgyan, V. N.; Ignatovitch, L. M.; Lukevics, E. *J. Organomet. Chem.* **1985**, *284*, C31–C32.

(70) Stang, P. J.; White, M. R. *J. Am. Chem. Soc.* **1981**, *103*, 5429–5433.

(71) Gilman, H.; Leeper, R. W. *J. Org. Chem.* **1951**, *16*, 466–475.

(72) Orndorff, W. R.; Tabern, D. L.; Dennis, L. M. *J. Am. Chem. Soc.* **1927**, *49*, 2512–2516.

(73) Seyferth, D. *J. Am. Chem. Soc.* **1958**, *80*, 1336–1337.

(74) We thank Prof. S. R. Wilson of New York University for his advice and details on the handling of this bromide and its conversion to the Grignard reagent.[75]

(75) Wilson, S. R.; Shedrinsky, A. *J. Org. Chem.* **1982**, *47*, 1983–1984. Wilson, S. R.; Shedrinsky, A.; Haque, M. S. *Tetrahedron* **1983**, *39*, 895–903.

(cmplx m, $SiCH_2$), 0.11 (s, SiMe). The peroxide decomposed readily, as cited.[76] A 0.66 M solution in *tert*-butylbenzene largely decomposed to CO_2 (IR, 2330) and, presumably, β-(trimethylsilyl)ethyl β-(trimethylsilyl)propionate (IR, 1740) after 24 h at 25 °C.

Tris[γ-(trimethylsilyl)-*n*-propyl]arsine was prepared from **γ-(trimethylsilyl)-*n*-propyl bromide.** The latter compound was made by treatment of γ-(trichlorosilyl)-*n*-propyl bromide (Petrarch) with methylmagnesium bromide in ether as described for the corresponding butyl case:[77] 92%; bp (Kugelrohr) 60–63 °C at 5 mm (lit.[78] bp 70 °C at 25 mm); IR (neat) 1250, 850 (Me_3Si); ^1H NMR ($CDCl_3$, no TMS) 3.35 (t, J = 7 Hz, CH_2Br), 2.06–1.50 (cmplx m, β-CH_2), 0.73–0.40 (cmplx m, $SiCH_2$), 0.01 (s, SiMe). The bromide (175 mmol) was converted into its Grignard reagent in dry THF (125 mL) in the usual way. To the cooled Grignard reagent under nitrogen was added with stirring $AsCl_3$ (9.06 g, 4.2 mL, 50 mmol) in benzene (6 mL). The solution turned brown as salts precipitated. After 12 h at 25 °C the solution was heated at reflux for 4.5 h, chilled, and processed in a glovebag under nitrogen as detailed above for $(Me_3SiCH_2CH_2)_3As$. Upon addition of pentane to the oily residue obtained by such processing, crystalline **bis[γ-(trimethylsilyl)-*n*-propyl]chloroarsine** precipitated: 15%; mp (from pentane/hexane) 118–121 °C; positive $AgNO_3$ test; IR (KBr) 1250, 850 (Me_3Si); ^1H NMR (acetone-d_6) 3.05–2.67 (cmplx m, CH_2As), 2.24–1.62 (cmplx m, β-CH_2), 0.90–0.57 (cmplx m, $SiCH_2$), 0.10 (s, SiMe). Anal. Calcd for $C_{12}H_{30}AsClSi_2$: C, 42.28; H, 8.87. Found: C, 42.21; H, 8.98. The filtrate was freed from pentane and distilled in a Kugelrohr apparatus at 0.1 mm. The first fraction (bath at 40–50 °C) was the dimeric coupling product, **1,6-bis(trimethylsilyl)hexane**: 16%; ^1H NMR ($CDCl_3$, no TMS) 1.50–1.17 (sharp m, 2,3,4,5-CH_2's), 0.70–0.33 (brd m, $SiCH_2$'s), 0.0 (s, SiMe). The $(Me_3SiCH_2CH_2CH_2)_3As$ was collected next (bath at 100–110 °C) as a colorless oil: 63%; IR 1250, 850 (Me_3Si); ^1H NMR ($CDCl_3$, no TMS) 1.50–1.27 (sharp m, β,γ-CH_2's), 0.70–0.26 (cmplx m, α-CH_2), −0.06 (s, SiMe); MS (m/e), P calcd 420.20, found 420.15. This arsine also oxidized in air. Its mercurichloride derivative was prepared by mixing equimolar amounts of the reactants in hot absolute ethanol and chilling: white needles; mp 138.5–140 °C. Anal. Calcd for $C_{18}H_{45}AsCl_2HgSi_3$: C, 31.23; H, 6.55. Found: C, 30.59; H, 6.45. For the laser study, higher purity material was collected by preparative GC (5% OV-101 column at 230 °C): MS (m/e), P + 1, P + 2, P + 3% calcd: 35.50, 15.96, 3.67, respectively. Found: 37.0, 16.4, 2.7.

γ-(Trimethylsilyl)-*n*-butyryl peroxide was prepared from γ-(trimethylsilyl)-*n*-butyronitrile, which was obtained by reaction of methyllithium with (γ-cyano-*n*-propyl)dimethylchlorosilane (Petrarch) in 95% crude yield: IR (neat) 2245 (CN), 1255, 865 (Me_3Si); ^1H NMR ($CDCl_3$, TMS) 2.33 (t, J = 7 Hz, CH_2CN), 1.77–1.40 (cmplx m, β-CH_2), 0.87–0.53 (cmplx m, $SiCH_2$), 0.10 (s, SiMe). Hydrolysis to **γ-(trimethylsilyl)-*n*-butyric acid** (71%; bp 112–114 °C at 13 mm (lit.[79] bp 117–119 °C at 15 mm); IR (neat) 3700–2300, 1715 (COOH), 1260, 850 (Me_3Si)) and conversion of the acid to its acid chloride (95%; IR (CCl_4) 1795 (CO)) were accomplished as reported.[79] The desired peroxide was made by the literature method[76] employed for β-(trimethylsilyl)propionyl peroxide: colorless oil, not distilled; 85% pure by iodometric analysis; IR (CCl_4) 1811, 1728 (CO), 1260, 845 (Me_3Si). Attempts to prepare this peroxide by other methods[80,81] gave impure material.

Products. The products from $Me_3SiCH_2CH_2Br$ and $Me_3SiCH_2CH_2CH_2Br$ reduction by *n*-Bu_3GeH were isolated by GC and shown to be $Me_3SiCH_2CH_3$ and $Me_3SiCH_2CH_2CH_3$, respectively, by authentication with samples prepared by a literature method.[82] The reduction of Me_3SiCH_2Br by *n*-Bu_3SnH had been shown earlier[35] to afford Me_4Si.

Laser flash photolysis studies were carried out in the usual manner.[12,13,16,21,28,49,83]

Rate and relative rate studies of the reduction of bromides by *n*-Bu_3SnH were carried out in degassed, sealed NMR tubes at 33 °C.

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Registry No. **1**-Br, 18243-41-9; $\mathbf{1}^\bullet$, 19469-02-4; **2-Br**, 18156-67-7; $\mathbf{2}^\bullet$, 36058-43-2; **3**-Br, 10545-34-3; $\mathbf{3}^\bullet$, 111351-52-1; $CH_3CH_2CH_2CH_2Br$, 109-65-9; *n*-Bu_3GeH, 998-39-0; $CH_3^\bullet$, 2229-07-4; $CH_3CH_2CH_2CH_2^\bullet$, 2492-36-6; *n*-Bu_3SnH, 688-73-3; *n*-Bu_3GeBr, 2117-37-5; $(Me_3SiCH_2)_3As$, 18138-47-1; $(Me_3SiCH_2CH_2)_3As$, 111351-53-2; $AsCl_3$, 7784-34-1; $Me_3SiCH_2CH_2CH_2CH_2SiMe_3$, 18001-81-5; $(Me_3SiCH_2CH_2)_2AsCl$, 111351-54-3; $(Me_3SiCH_2CH_2CH_2)_3As$, 111351-55-4; $Cl_3SiCH_2CH_2CH_2Br$, 13883-39-1; $CH_2{=}CHCH_2CH_2SiMe_2CH_2^\bullet$, 78957-28-5; $CH_2{=}CHCH_2SiMe_2CH_2CH_2^\bullet$, 111379-07-8; $CH_2{=}CHSiMe_2CH_2CH_2CH_2^\bullet$, 78957-29-6; $CH_2{=}CHCH_2CH_2CH_2CH_2^\bullet$, 16183-00-9; $CH_2{=}CHCH_2CH_2CMe_2CH_2^\bullet$, 71880-21-2; $(Me_3SiCH_2CH_2CH_2)_2AsCl$, 111379-08-9; $Me_3SiCH_2CH_2CH_2CH_2CH_2CH_2SiMe_3$, 13083-96-0; $Me_3SiCH_2CH_2CH_2C(O)OOH$, 111351-56-5; $Me_3SiCH_2CH_2CH_2CN$, 18301-86-5; $Me_2Si(Cl)CH_2CH_2CH_2CN$, 18156-15-5; $Me_3SiCH_2CH_2CH_2CO_2H$, 2345-40-6; $Me_3SiCH_2CH_2CH_3$, 3510-70-1; $Me_3SiCH_2CH_3$, 3439-38-1.

Supplementary Material Available: Table VII, giving detailed kinetic data for the reactions of $\mathbf{1}^\bullet$ and $\mathbf{3}^\bullet$ with *n*-Bu_3SnH (1 page). Ordering information is given on any current masthead page.

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(76) Brevnova, T. N.; Rachkova, O. F.; Vyazankin, N. S. *Zh. Obshch. Khim.* **1970**, *40*, 1760–1762. In this preparation, these workers used 58% H_2O_2, but the more available 30% strength used in the present study seemed equally effective.

(77) Čapka, M.; Schraml, J.; Jancke, H. *Collect. Czech. Chem. Commun.* **1978**, *43*, 3347–3355.

(78) Sommer, L. H.; Van Strein, R. E.; Whitmore, F. C. *J. Am. Chem. Soc.* **1949**, *71*, 3056–3060.

(79) Razuvaev, G. A.; Brevnova, T. N.; Cherepinnikova, N. F.; Ratushnaya, S. Kh. *Zh. Obshch. Khim.* **1976**, *46*, 857–861.

(80) Staab, H. A.; Rohr, W.; Graf, F. *Chem. Ber.* **1965**, *98*, 1122–1127.

(81) Webb, P. G.; Kampmeier, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3730–3738.

(82) Whitmore, F. C.; Sommer, L. H.; DiGiorgio, P. A.; Strong, W. A.; Van Strien, R. E.; Bailey, D. L.; Hall, H. K.; Pietrusza, E. W.; Kerr, G. T. *J. Am. Chem. Soc.* **1946**, *68*, 475–481.

(83) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7753.