and α-methylnaphthalene. α-Isopropylnaphthalene was prepared in two steps via reaction of the Grignard reagent of α-bromonaphthalene with acetone, followed by reduction of the resulting carbinol according to a published literature procedure.[15] A sample of 1,9-ethyleneanthracene was provided by Prof. Laren Tolbert (Georgia Institute of Technology). Carbon tetrachloride was slurried with potassium hydroxide for 24 h, decanted, and fractionally distilled from phosphorus pentoxide. The middle portion was stored over molecular sieves. NBS (Aldrich) was recrystallized from water and dried in vacuo before use. Gas chromatographic analyses were performed on a Hewlett-Packard HP 5890A instrument equipped with both FID and TCD detectors and an HP 3393A reporting integrator. Nuclear magnetic resonance spectra were recorded on a 270-MHz Bruker FT NMR spectrometer.

Competition Experiments. Competitive brominations (NBS/CCl$_4$) were carried out as described earlier.[1] Reaction mixtures were analyzed by GLC (vs chlorobenzene as internal standard) in triplicate. Relative rate constants were calculated by $k_A/k_B = \ln (A_o/A)/\ln (B_o/B_f)$, where the subscripts "o" and "f" refer to the initial and final concentrations of substrate, respectively. Mass balances were nearly quantitative, although elimination products were detected by NMR and GCMS in the reactions involving α-isopropylnaphthalene, 1,8-ethylenenaphthalene, and 1,9-ethyleneanthracene.

Theoretical. Semiempirical MO calculations were performed using the AM1 approximation developed by Dewar et al.[4] and implemented through MOPAC Version 5.0 (QCPE 455). Full geometry optimizations were performed on the parent hydrocarbon. For the open-shell species, geometries were optimized using UHF, followed by a single-point calculation using the half-electron approximation.[16,17]

Acknowledgment. We gratefully acknowledge and thank the Thomas F. Jeffress and Kate Miller Jeffress Memorial Trust Fund for financial support. We also thank Prof. Laren Tolbert (Georgia Tech) for the sample of 1,9-ethyleneanthracene and for helpful suggestions.

Registry No. 6, 496-11-7; 7, 83-32-9; 8, 641-48-5; Br, 10097-32-2; PhEt, 100-41-4; α-methylnaphthalene, 90-12-0; α-ethylnaphthalene, 1127-76-0; α-isopropylnaphthalene, 6158-45-8; 9-ethylanthracene, 605-83-4.

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(15) Calvert, D. J.; De La Mare, P. B. D.; Ogawa, T.; Yamamoto, H.; Suzuki, H. *Gazz. Chim. Ital.* 1987, *117*, 357–61.

(16) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* 1978, *100*, 784.

(17) Clark, T. *Handbook of Computational Chemistry: A Practical Guide to Chemical Structure and Energy Calculations*; Wiley: New York, 1985.

Rate Constants and Arrhenius Parameters for the Reactions of Some Carbon-Centered Radicals with Tris(trimethylsilyl)silane

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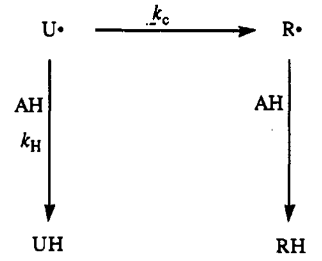
Rate constants for the reactions of some carbon-centered radicals with (Me$_3$Si)$_3$SiH have been measured over a range of temperatures by using competing unimolecular radical reactions as timing devices. For example, the rate constants (at 298 K) are 3.7, 1.4, and 2.6 × 10^5 M^{-1} s^{-1} from primary, secondary, and tertiary alkyl radicals, respectively. Comparison of the radical trapping abilities of tri-*n*-butylstannane and tris(trimethylsilyl)silane is discussed. The use of 1,1-dimethyl-5-hexenyl cyclization as a radical clock has been recalibrated by using new data and data from the literature.

Introduction

Free radicals are of considerable importance in the development of organic chemistry, and many methodologies in radical-based synthesis employ tributyltin hydride.[2-4] It has recently been shown that tris(trimethylsilyl)silane is a valuable reducing agent for a variety of organic substrates.[5,6] This reagent has proved to be an attractive alternative to tributyltin hydride for the majority of these reactions although in a few cases the two reagents can complement each other. The key step in these straightforward radical-chain reduction reactions,[5,6] as well as in those processes where their use as a mediator for the formation of carbon–carbon bonds[7] via an inter- or intramolecular addition, is

$$R^\bullet + X_3MH \rightarrow RH + X_3M^\bullet \qquad (1)$$

Scheme I



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(2) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: Oxford, 1986.

(3) Neumann, W. P. *Synthesis* 1987, 665 and references cited therein.

(4) Curran, D. P. *Synthesis* 1988, 417 and 489.

(5) Chatgilialoglu, C. in *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; Kluwer: Dordrecht, 1989; pp 115–127.

(6) Chatgilialoglu, C.; Griller, D.; Lesage, M. *J. Org. Chem.* 1988, *53*, 3641. Ballestri, M.; Chatgilialoglu, C.; Clark, K. B.; Griller, D.; Giese, B.; Kopping, B. *J. Org. Chem.* 1991, *56*, 678.

(7) Chatgilialoglu, C.; Giese, B.; Kopping, B. *Tetrahedron Lett.* 1990, *31*, 6013. Giese, B.; Kopping, B.; Chatgilialoglu, C. *Tetrahedron Lett.* 1989, *30*, 681.

where X_3MH = n-Bu_3SnH or $(Me_3Si)_3SiH$.

In 1981, rate constants and Arrhenius parameters for the reaction of some carbon-centered radicals with n-Bu_3SnH were determined using laser flash photolytic techniques.[8] The several hundred citations of this article over the last decade undoubtedly indicate the importance of these widely used data in understanding and in programming free-radical reactions. In this study, we have used competing unimolecular radical reactions as timing devices (free-radical clocks[9]) to investigate the rates of primary, secondary, tertiary alkyl, and phenyl radicals toward tris(trimethylsilyl)silane.

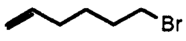
Results

Method. An indirect procedure for measuring the rate constant of a radical-molecule reaction involves a competition between this process and a unimolecular path of the radical.[10] For example, absolute values of the rate constant for H atom abstraction from a hydride (AH) by an alkyl radical U$^\bullet$ can be obtained, providing that conditions can be found in which an unrearranged radical U$^\bullet$ either reacts with AH or rearranges to R$^\bullet$ with a known rate constant (Scheme I).

If the hydride concentration remains essentially constant under the experimental conditions, then the following relation holds:[11]

$$\frac{k_c}{k_H} = [AH]\frac{[RH]}{[UH]} \tag{2}$$

Bromides 1–4 were chosen as precursors of carbon-centered radicals since their cyclization reactions, under free-radical conditions, have been studied in some detail (see infra).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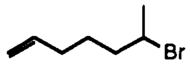
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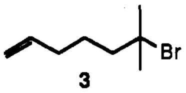
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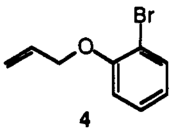
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Reaction of 5-Hexenyl with $(Me_3Si)_3SiH$. This primary alkyl radical was formed from the corresponding alkenyl bromide and tris(trimethylsilyl)silane by a thermally initiated or photoinitiated radical-chain reaction in n-octane. The two major hydrocarbon products were 1-hexene and methylcyclopentane, the relative concentrations of which varied in the expected manner at each temperature as the concentration of silane was changed. The reactions of interest are shown in Scheme I, where U$^\bullet$ and R$^\bullet$ represent the 5-hexenyl and cyclopentylmethyl radical, respectively. Minor quantities of cyclohexane were also formed, its concentration relative to methylcyclopentane increasing with temperature from 0.8% (relative to methylcyclopentane) at 258 K to 2.7% at 393 K.[12]

Table I. Kinetic Data for the Reaction of 6-Bromohex-1-ene with $(Me_3Si)_3SiH$ in n-Octane at Various Temperatures

T, K	$[(Me_3Si)_3SiH]$,^{a} M	k_c/k_H,^{b} M
288	0.474–2.129	0.567 ± 0.045
303	0.656–1.638	0.710 ± 0.087
333	0.571–1.811	1.077 ± 0.040
363	0.610–1.502	1.485 ± 0.061
393	0.425–1.891	1.555 ± 0.088

[a] Range of concentration employed. [b] Errors correspond to 1 standard deviation.

Table II. Kinetic Data for the Reaction of 6-Bromohept-1-ene with $(Me_3Si)_3SiH$ in n-Tetradecane at Various Temperatures

T, K	$[(Me_3Si)_3SiH]$,^{a} M	k_c'/k_H,^{b} M	k_c/k_H,^{b} M
288	0.651–1.954	0.600 ± 0.060	0.162 ± 0.021
303	0.555–1.929	0.926 ± 0.025	0.244 ± 0.011
333	0.574–2.063	1.160 ± 0.041	0.372 ± 0.019
363	0.539–2.240	1.472 ± 0.074	0.511 ± 0.033
393	0.789–2.036	1.835 ± 0.053	0.760 ± 0.044

[a] Range of concentration employed. [b] Errors correspond to 1 standard deviation.

Mean values of the k_c/k_H ratio were obtained at different silane concentrations according to eq 2. The data are summarized in Table I, while the detailed results of the individual experiments are available as supplementary material. Analysis of these data yields the Arrhenius expression

$$\log (k_c/k_H)(M) = (1.56 \pm 0.36) - (2.38 \pm 0.55)/\theta \tag{3}$$

where $\theta = 2.3RT$ kcal mol^{-1} and the errors correspond to 95% confidence limits.[13] The absolute value of the rate constants for H atom abstraction from $(Me_3Si)_3SiH$ by the primary alkyl radical, i.e., k_H, can be obtained by combining eq 3 with the Arrhenius equation for the 5-hexenyl cyclization:[14]

$$\log k_H(M^{-1}\ s^{-1}) = (8.86 \pm 0.68) - (4.47 \pm 0.92)/\theta \tag{4}$$

In a similar manner, we measured the rate constant for deuterium atom abstraction from $(Me_3Si)_3SiD$ by the 5-hexenyl radical and found it to be $k_D = 5.87 \times 10^5$ M^{-1} s^{-1} at 363 K. Detailed results of this experiment are also available as supplementary material.

Reaction of 1-Methyl-5-hexenyl with $(Me_3Si)_3SiH$. This secondary alkyl radical was formed from the corresponding bromide 2 and tris(trimethylsilyl)silane by a thermal-initiated or photoinitiated, radical-chain reaction in n-tetradecane. The three major hydrocarbon products were hept-1-ene, and *cis*- and *trans*-1,2-dimethylcyclopentane in agreement with recent work of Ingold and coworkers,[15] who have calibrated the 1-methyl-5-hexenyl radical clock with precision. The reactions of interest are shown in Scheme II. Because we were unable to achieve separation of *cis*-1,2-dimethylcyclopentane and methylcyclohexane, the k_c' value represents the sum of the two processes. Mean values of the k_c/k_H and k_c'/k_H ratio obtained at different silane concentrations and varying extents of reaction at each temperature are summarized in Table II. Detailed results of the individual experiments

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(8) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

(9) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(10) For reviews, see: 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. Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.

(11) This technique has been quite widely employed to determine the rate constants and Arrhenius parameters either for the unimolecular rearrangement or the radical-molecule reaction.

(12) As expected, see: Walling, C.; Cooley, J. H.; Poramas, A. A.; Racah, E. J. *J. Am. Chem. Soc.* **1966**, *88*, 5361.

(13) Errors correspond to 95% confidence limits (twice the standard deviation) but include only random and not systematic errors. It is worthy to point out that the high precision of the equation does not necessarily translate into similarly accurate kinetic values.

(14) The temperature-dependent function for cyclization of 5-hexenyl is as follows:[8] $\log k_c(s^{-1}) = (10.42 \pm 0.32) - (6.85 \pm 0.42)/\theta$, where $\theta = 2.3RT$ kcal mol^{-1}.

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

Scheme II

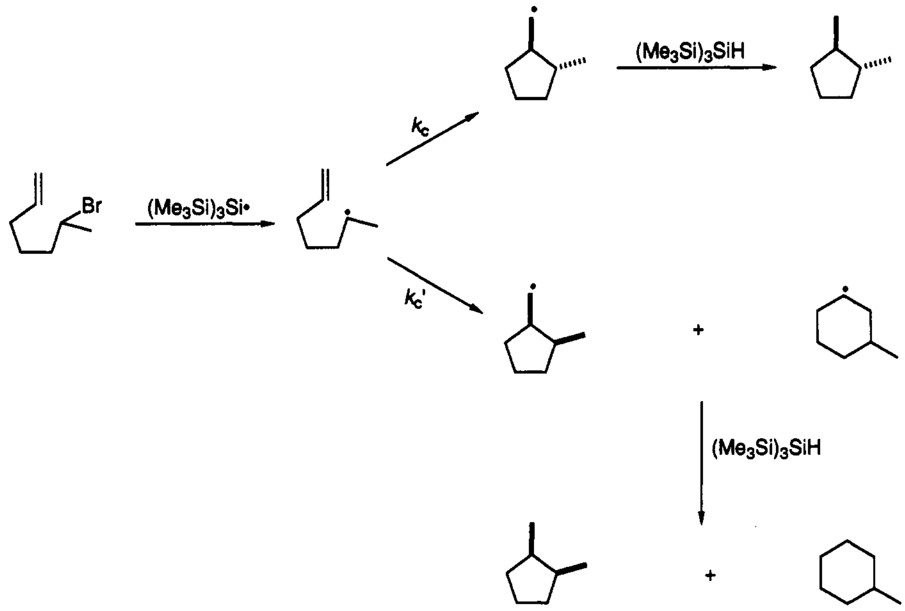


Table III. Kinetic Data for the Reaction of 6-Bromo-6-methylhept-1-ene with $(Me_3Si)_3SiH$ in *n*-Tetradecane at Various Temperatures

T, K	$[(Me_3Si)_3SiH]$,[a] M	k_c/k_H,[b] M
288	0.848–2.009	1.209 ± 0.193
303	0.545–2.126	1.220 ± 0.143
333	0.694–1.889	1.855 ± 0.082
363	0.602–2.224	2.820 ± 0.035
393	0.587–1.746	3.661 ± 0.146

[a] Range of concentration employed. [b] Errors correspond to 1 standard deviation.

are available as supplementary material. Analysis of these experimental data yields the Arrhenius parameters

$$\log (k_c'/k_H)(\mathrm{M}) = (1.50 \pm 0.35) - (2.21 \pm 0.53)/\Theta \quad (5)$$

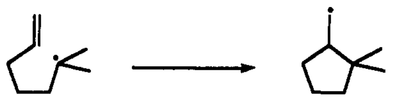
$$\log (k_c/k_H)(\mathrm{M}) = (1.63 \pm 0.22) - (3.15 \pm 0.34)/\Theta \quad (6)$$

where $\Theta = 2.3RT$ kcal mol^{-1} and the errors correspond to 95% confidence limits.[13] Combination of eqs 5 and 6 with Arrhenius equations for cis and trans cyclization reactions[16] yields, respectively, the relationships

$$\log k_H(\mathrm{M}^{-1}\,\mathrm{s}^{-1}) = (8.29 \pm 0.59) - (4.29 \pm 0.79)/\Theta \quad (7)$$

$$\log k_H(\mathrm{M}^{-1}\,\mathrm{s}^{-1}) = (8.29 \pm 0.48) - (4.29 \pm 0.63)/\Theta \quad (8)$$

Reaction of 1,1-Dimethyl-5-hexenyl with $(Me_3Si)_3SiH$. Bromide 3 was employed as precursor using the technique described above to study this reaction. A GC analysis of the reaction mixture showed three products: 6-methyl-1-heptene, 1,1,2-trimethylcyclopentane, and 1,1-dimethylcyclohexane. The kinetic treatment was based on the expected mechanism, illustrated in Scheme I, where U$^•$ and R$^•$ represent radicals 5 and 6, respectively.



5 6 (9)

Table IV. Kinetic Data for the Cyclization of the 1,1-Dimethyl-5-hexenyl Radical[a]

T, K	k_c, s^{-1}	ref
179	483	15
182	401	15
183	564	15
338	1.37×10^{6b}	17
363	1.89×10^6	this work
393	3.16×10^6	this work

[a] The temperature employed in the kinetic ESR studies (ref 15) was 170–193 K; however, we take in consideration the values measured in the middle of the temperature range being probably more reliable. [b] This rate constant was calculated from k_c/k_{SnH} = 0.41 M and $k_{SnH} = 3.33 \times 10^6$ M^{-1} s^{-1}. The latter rate constant was calculated from the Me$_3$C$^•$ + *n*-Bu$_3$SnH reaction given in ref 8.

Mean values of the k_c/k_H ratio obtained at different silane concentrations and varying extents of the reaction at each temperature are summarized in Table III. The results of each individual experiment are available as supplementary material. The data in Table III yield the Arrhenius equation

$$\log (k_c/k_H)(\mathrm{M}) = (1.97 \pm 0.34) - (2.56 \pm 0.51)/\Theta \quad (10)$$

where $\Theta = 2.3RT$ kcal mol^{-1} and the errors correspond to 95% confidence limits.[13]

Calibration of the 1,1-Dimethyl-5-hexenyl Radical Clock. The cyclization of tertiary radical 5 to radical 6 has been studied by two methods.[15,17] One high-temperature rate constant was determined by Beckwith et al.[17] in competitive studies using *n*-Bu$_3$SnH. At low temperatures (170–193 K) the cyclization was studied by Ingold and co-workers directly by kinetic ESR methods.[15] Therefore, the temperature-dependent function based on these data for the cyclization of the 1,1-dimethyl-5-hexenyl radical is not very reliable.

Here, we measured two more additional high-temperature rate constants in competitive studies using *n*-Bu$_3$SnH. Radical 5 was formed from the corresponding bromide 3 and *n*-Bu$_3$SnH by a thermally initiated radical chain reaction in *n*-tetradecane. Mean values of the k_c/k_{SnH} ratio were obtained at different stannane concentrations ac-

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[16] The temperature-dependent function for cyclization of 1-methyl-5-hexenyl is as follows:[15] $\log k_c'(\mathrm{s}^{-1}) = (9.79 \pm 0.24) - (6.50 \pm 0.26)/\Theta$ $\log k_c(\mathrm{s}^{-1}) = (9.92 \pm 0.26) - (7.44 \pm 0.29)/\Theta$, where $\Theta = 2.3RT$ kcal mol^{-1}.

[17] Beckwith, A. L. J.; Blair, I. A.; Philipou, G. *Tetrahedron Lett.* 1974, 2251.

Table V. Kinetic Data for the Reaction of Allyl *o*-Bromophenyl Ether with $(Me_3Si)_3SiH$ in *n*-Octane at Various Temperatures

T, K	$[(Me_3Si)_3SiH]$,[a] M	k_c/k_H,[b] M
289	0.93–2.67	29.49 ± 3.28
303	0.97–2.49	31.64 ± 1.45
333	1.38–2.56	41.15 ± 7.32
363	1.37–2.75	51.80 ± 3.43
393	0.77–2.45	58.33 ± 3.20

[a] Range of concentration employed. [b] Errors correspond to 1 standard deviation.

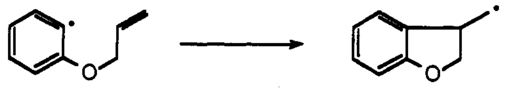
cording to eq 2 and found to be 0.420 and 0.513 M (at 363 and 393 K, respectively), which, on combining with k_{SnH},[18] yield the rate constants for cyclization. Table IV contains these new data together with literature data. Analysis of all experimental data yields the Arrhenius expression

$$\log k_c(s^{-1}) = (9.90 \pm 0.25) - (6.00 \pm 0.26)/\Theta \quad (11)$$

where $\Theta = 2.3RT$ kcal mol^{-1} and the errors correspond to 95% confidence limits.[13,19] Combination of eqs 10 and 11 yield the Arrhenius equation below for hydrogen atom abstraction from tris(trimethylsilyl)silane by tertiary alkyl radicals.

$$\log k_H(M^{-1}\ s^{-1}) = (7.93 \pm 0.59) - (3.44 \pm 0.77)/\Theta \quad (12)$$

Reaction of *o*-(Allyloxy)phenyl with $(Me_3Si)_3SiH$. When allyl *o*-bromophenyl ether was mixed with tris(trimethylsilyl)silane in *n*-octane in the presence of a free-radical initiator, a clean reaction ensued and 3-methyl-2,3-dihydrobenzofuran was obtained as the major product. Minor quantities of allyl phenyl ether were also formed. The reactions of interest are shown in Scheme I, where U• and R• represent radicals 7 and 8, respectively.


(13)

7 8

Mean values of the k_c/k_H ratio obtained at different silane concentrations and varying extents of reaction at each temperature are summarized in Table V. The results of each individual experiment are available as supplementary material. Analysis of these data yields the relationship

$$\log (k_c/k_H)(M) = (2.64 \pm 0.11) - (1.56 \pm 0.16)/\Theta \quad (14)$$

Unfortunately, reliable absolute rate constants for the cyclization 7 → 8 are not available.[20] We are, therefore, unable to obtain rate constants for H atom abstraction from $(Me_3Si)_3SiH$ by the ortho-substituted phenyl radical. However, combining eq 14 with the analogous equation[20] for n-Bu_3SnH yields the following relationship for the *o*-(allyloxy)phenyl radical

$$\log (k_{SnH}/k_{SiH}) = 0.5_5 - 0.0_5/\Theta \quad (15)$$

where k_{SnH} and k_{SiH} represent the rate constants of H atom abstraction by radical 5 from n-Bu_3SnH and $(Me_3Si)_3SiH$, respectively. From eq 15 we calculate that k_{SnH} is ca. 3 times faster than k_{SiH} at room temperature.

Table VI. Kinetic Parameters for the Reaction of Alkyl Radicals with $(Me_3Si)_3SiH$ and n-Bu_3SnH

alkyl radical	hydride	log *A* M^{-1} s^{-1}	E_a kcal mol^{-1}	k_H^{298} 10^{-5} M^{-1} s^{-1}
primary[a]	$(Me_3Si)_3SiH$	8.86 ± 0.68	4.47 ± 0.92	3.82
primary[b]	n-Bu_3SnH	9.07 ± 0.24	3.69 ± 0.32	23.12
secondary[c]	$(Me_3Si)_3SiH$	8.29 ± 0.59	4.29 ± 0.79	1.38
secondary[d]	n-Bu_3SnH	8.71 ± 0.37	3.47 ± 0.49	14.65
tertiary[e]	$(Me_3Si)_3SiH$	7.93 ± 0.59	3.44 ± 0.77	2.55
tertiary[f]	n-Bu_3SnH	8.43 ± 0.14	2.95 ± 0.19	18.48

[a] 5-Hexenyl; this work. [b] Combined data for ethyl and *n*-butyl radical; ref 8. [c] 1-Methyl-5-hexenyl; this work. [d] Isopropyl; ref 8. [e] 1,1-Dimethyl-5-hexenyl; this work. [f] *tert*-Butyl; ref 8.

Discussion

Kinetic parameters for the reaction of primary, secondary, and tertiary alkyl radicals with tris(trimethylsilyl)silane are compared in Table VI with analogous parameters for their reaction with tri-*n*-butyltin hydride.[24] The silane is a slightly less reactive hydrogen donor than the stannane, presumably because the Si–H bond is 5 kcal mol^{-1} stronger than the comparable Sn–H bond.[25] This difference in bond strength manifests itself above all in enthalpies of activation; i.e., the larger activation energies for $(Me_3Si)_3SiH$ must be due to the fact that such reactions are less exothermic. The Arrhenius preexponential factors all lie in the expected range and show the anticipated decrease with increasing steric hindrance of the attacking alkyl radical.

However, the fact that $(Me_3Si)_3SiH$ is only ca. 10 times less reactive than n-Bu_3SnH toward alkyl radicals demonstrates that this silane is good both for straightforward reductions[6,26] and for carbon–carbon bond formation,[7] as the alkyl radical should add to a multiple bond prior to reaction with the hydrogen donor. The rate constants for the reaction of an aryl radical with silane is only 3 times slower than stannane, the reason presumably being that these reactions are in the proximity of diffusion-controlled rates. The deuterium kinetic isotope effect for the reaction of primary alkyl radicals with $(Me_3Si)_3SiH$ is found to be 2.3 (at 363 K) and is similar to the value of 2.3 (at 300 K)

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[18] We calculate $k_{SnH} = 4.51 \times 10^6$ and 6.16×10^6 M^{-1} s^{-1} at 363 and 393 K respectively from the Arrhenius parameters for the $Me_3C^\bullet$ + n-Bu_3SnH reaction given in ref 8.

[19] A reviewer pointed out that eq 11 might imply too high a degree of accuracy owing to the large $1/T$ range and the uneven distribution of points in the range. In fact (cf. Table IV), these are two clusters of three points each at the two sides of the interval. We share the reviewer's comment; nevertheless, we feel that our treatment of the experimental data is the only one adequate and gives sufficiently reliable results.

[20] In 1985, Ingold and co-workers[21] reported rate constants and Arrhenius parameters for the reaction of the phenyl radical with tri-*n*-butyltin hydride using benzoyl peroxide with light as the source of radical formation. These kinetic data were later used by Beckwith and co-workers[22] to calibrate the cyclization of some aryl radicals bearing unsaturated ortho substituents, including reaction 13. In subsequent papers, Ingold and co-workers[23] showed that $ArCO_2^\bullet$ radicals, generated from aroyl peroxides, also react rapidly with n-Bu_3SnH, concluding that in their early work[21] they were not monitoring a "clean" Ph• + n-Bu_3SnH reaction. Therefore, rate constants for the cyclization 7 → 8 are not available, as the rate constant for the phenyl radical/tin hydride reaction still remains to be determined.

[21] 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.

[22] Abeywickreyma, A. N.; Beckwith, A. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 464.

[23] Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2877 and 2886.

[24] The rate constants for the reaction of primary and tertiary alkyl radicals with Et_3SiH are 7×10^3 and 3×10^3 M^{-1} s^{-1} at 323 K, respectively (see: Newcomb, M.; Park, S. U. *J. Am. Chem. Soc.* **1986**, *108*, 4132).

[25] Kanabus-Kaminska, J. M.; Hawari, J. A.; Griller, D.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1987**, *109*, 5267.

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for the analogous reaction with stannane.[8]

Finally, we are confident that the kinetic data reported in this work will find wide and general use in mechanistic and synthetic applications.

Experimental Section

Materials. Tris(trimethylsilyl)silane and 6-bromohex-1-ene (1) were obtained commercially (Fluka) and used as received. The $(Me_3Si)_3SiD$ was synthesized by reduction of the corresponding chloride with $LiAlD_4$.[27] 6-Bromohept-1-ene (2) and 6-bromo-6-methylhept-1-ene (3) were prepared by reacting 6-oxohept-1-ene with $LiAlH_4$ and MeMgBr, respectively, and consecutive reaction with 1,2-bis(diphenylphosphino)ethane tetrabromide.[28] 6-Oxohept-1-ene was obtained from ethyl acetoacetate and 4-bromobut-1-ene. Allyl *o*-bromophenyl ether (4) was made from allyl bromide and *o*-bromophenol in the usual way.[29] All compounds in this work were at least 97% pure. The purity was checked by GC and/or NMR.

General Procedure. *n*-Octane or *n*-tetradecane containing a small amount of *n*-decane as an internal GC standard was used as solvent. Tris(trimethylsilyl)silane was added at concentrations between 0.5 and 2.2 M, and the bromides were added at a concentration of ca. 0.1 M. Samples of these reaction mixtures were degassed and sealed with rubber septa under argon in Pyrex ampules and were then thermolyzed or photolyzed. Reactions were initiated thermally at temperatures of 333, 363, and 393 K and photolytically at 288 and 303 K. The consumption of the bromides was varied from 5% up to 98%. Reaction times varied from 5 s to 2 min. The products of the reactions of 6-bromohex-1-ene (1), 6-bromo-6-methylhept-1-ene (3), and allyl *o*-bromophenyl ether (4) were analyzed by GC using a 25 m × 0.25 mm SE-54-DE column (Macherey und Nagel) with temperature programming from 40 to 300 °C using a Carlo Erba GC 6000 Vega Series 2 chromatograph. In the case of 6-bromohept-1-ene (2), we used a 25 m × 0.25 mm CW20M-DF column (Macherey und Nagel) with temperature programming from 40 to 200 °C. The hydrocarbon products of interest were identified by comparison of their retention times with authentic material.

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Supplementary Material Available: Schemes III–VI and Tables VII–XI giving reactions of interest, kinetic expressions, and detailed product ratios (12 pages). Ordering information is given on any current masthead page.

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Mechanistic Analysis of the Reactions of (Pentafluorophenyl)nitrene in Alkanes

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Photolysis of pentafluorophenyl azide in *n*-butane, cyclopentane, or 2,3-dimethylbutane releases singlet (pentafluorophenyl)nitrene, which can insert into a CH bond, ring expand to a ketenimine, or undergo intersystem crossing (ISC) to the triplet state of the nitrene. In alkanes at 25 °C ring expansion is the major process, CH insertion is only modest, and ISC is unimportant. At temperatures below −78 °C, ISC is the dominant process. Differential activation parameters are derived and compared with those of phenyl azide

Introduction

Polyfluorinated arylnitrenes are unique amongst aromatic nitrenes in that they react with alkanes to give products of formal C–H insertion in fair to good yields.[1] The reaction was discovered by Banks and Sparkes, who studied the pyrolysis of various polyfluorinated aryl azides in alkanes.[2] The photochemical initiation of this reaction was reported much later by this laboratory.[3] The insertion of a nitrene into an unactivated CH bond is of great importance in photoaffinity labeling, a commonly used technique in biochemistry.[4] To further understand the fluorine effect we have studied the photochemistry of pentafluorophenyl azide 1 in alkanes as a function of temperature.

Table I. Absolute Yield of Products Formed upon Incomplete[a] Photolysis of 1

	n-butane			2,3-dimethylbutane	
T (°C)	**4**	**5**	*T* (°C)	**6**	**5**
25	7.3	0	25	16	0
25[b]	3.2	9.3	0	26	0
0	7.6	0	−25	23	8.2
−10	3.4	12	−50	20	20
−30	4.0	38	−78	7.8	40
−50	2.4	37			
−78	0	80			

[a] Typically, 10–15% of azide 1 was consumed during the photolysis. The absolute yields of products quoted are based on the percent conversion of the azide. [b] Triplet-sensitized photolysis using 4-methoxyacetophenone; a 2.3% yield of $C_6F_5NH_2$ was formed under these conditions; this product was not observed upon direct photolysis of 1.

Photochemistry of Pentafluorophenyl Azide in Alkanes. Photolysis of 1 at 25 °C in *n*-butane and 2,3-dimethylbutane produces the regiochemically pure prod-

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