Adjusting the Top End of the Alkyl Radical Kinetic Scale. Laser Flash Photolysis Calibrations of Fast Radical Clocks and Rate Constants for Reactions of Benzeneselenol

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Rate constants for 5-*exo* cyclizations of the 6,6-diphenyl-5-hexenyl radical (**1a**), the 1-methyl-6,6-diphenyl-5-hexenyl radical (**1b**), and the 1,1-dimethyl-6,6-diphenyl-5-hexenyl radical (**1c**) were measured by laser flash photolysis methods, and Arrhenius parameters for these cyclizations were determined. Relative rate constants for cyclizations of radicals **1** and reactions with benzeneselenol were determined by indirect kinetic methods, and the relative Arrhenius parameters for the competing reactions were combined with the parameters for the cyclization reactions to give absolute Arrhenius parameters for the PhSeH reactions. At 20 °C, PhSeH reacts with the 1°, 2°, and 3° radicals **1** with nearly the same rate constants, $(1.2 \pm 0.1) \times 10^9$ M^{-1} s^{-1}. Absolute Arrhenius parameters for reactions of PhSH and *t*-BuSH with the primary alkyl radical **1a** were calculated using literature values for the competition between cyclization of **1a** and reactions with the appropriate thiol and the absolute values for cyclization of **1a** determined in this work. The results suggest that rate constants for reactions of primary alkyl radicals with *t*-BuSH are about 20% smaller than those previously reported. In the case of PhSH, the results are in good agreement with one previously reported set of rate constants but about 35% smaller than another set of rate constants that was subsequently incorporated into fast alkyl radical kinetics. The rate constants for alkyl radical reactions calibrated by competition against reaction with PhSeH and PhSH apparently are 30−40% smaller than those previously reported, and the derived rate constants for the fast radical reactions should be adjusted. An especially noteworthy example is ring opening of the cyclopropylcarbinyl radical, the Arrhenius function for which was determined in part from PhSH trapping results. Using the adjusted rate constants for PhSH and recalculating the Arrhenius parameters for the cyclopropylcarbinyl radical ring opening gives $\log(k/s^{-1}) = (13.04_5 \pm 0.10) - (6.99 \pm 0.09)/\theta$ (kcal/mol, errors at 2σ); the rate constant at 20 °C of 6.7×10^7 s^{-1} is about 13% smaller than that previously calculated.

The determination of radical reaction rate constants by indirect, competition kinetic methods is well established.[1] A reaction with an unknown rate constant is allowed to compete with a reaction with a known rate constant, the basis reaction. The desired rate constant is calculated from the product distribution, the reagent concentrations, and the basis reaction rate constant. The method requires no special instrumentation and has been widely applied. Unimolecular radical reactions, commonly called "radical clocks",[1,2] are often used as basis reactions. In addition to the experimental simplification provided by using a radical clock as a basis reaction, some unimolecular alkyl radical reactions, such as cyclizations of 5-hexenyl radicals and ring openings of cyclopropylcarbinyl radicals, are well calibrated on an absolute scale and demonstrated to be insensitive to solvent polarity effects.[3−5]

Most of the available rate constants for alkyl radical reactions were determined indirectly and ultimately are placed on an absolute kinetic scale that is related to laser flash photolysis (LFP) measurements of the second-order rate constants for reactions of alkyl radicals with Bu_3SnH,[6,7] with PhSH,[8] and with nitroxyl radicals.[3,9−12] At the top end of the alkyl radical kinetic scale, aryl-substituted cyclopropylcarbinyl radical clocks with rate constants exceeding 1×10^{11} s^{-1} at ambient temperature have been calibrated against trapping by benzeneselenol.[13−16] Benzeneselenol, in turn, was calibrated by competition against the cyclopropylcarbinyl radical ring opening.[13,17]

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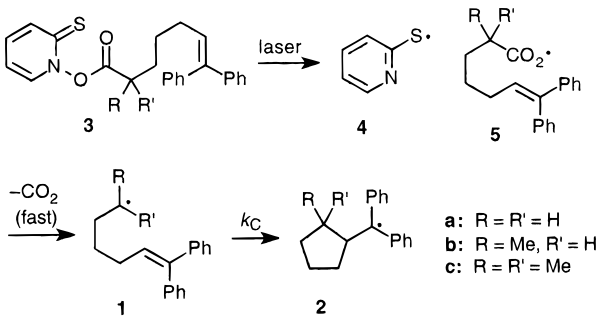
Scheme 1



In this work, we have expanded kinetic studies of PhSeH reactions and attempted to improve the accuracy of the top end of the alkyl radical kinetic scale. Rate constants were measured directly by LFP methods for 5-*exo* cyclizations of a series of 1°, 2°, and 3° alkyl radical clocks that react in the 10^7-10^8 s^{-1} range at ambient temperature. The clocks thus calibrated were used in indirect kinetic studies to provide rate constants for reactions with PhSeH. Because the relative Arrhenius parameters for reaction of one of the clocks with PhSH and *t*-BuSH were already known,[18] we were also able to check the accuracy of rate constants for reactions of these H-atom transfer agents with primary alkyl radicals. The results indicate that rate constants for primary alkyl radical reactions at the top end of the kinetic scale should be reduced somewhat, in the case of reactions calibrated against PhSeH trapping by about 35% at ambient temperatures.

Results and Discussion

LFP Calibration of Radical Clocks. The kinetics of cyclization of the 6,6-diphenyl-5-hexenyl radicals **1a**−**c** to the diphenylcyclopentylmethyl radicals **2a**−**c** were measured directly by LFP methods (Scheme 1). Radicals **1** were produced from the corresponding PTOC esters[19,20] **3** which were prepared from the appropriate carboxylic acids. Precursor **3a** was reported previously,[18] and the synthetic details for preparation of **3b** and **3c** are provided. Because PTOC esters are thermally unstable and sensitive to visible light, precursors **3** were characterized only by NMR spectroscopy.

PTOC esters were originally invented by Barton for synthetic applications,[19] but they have been used in a number of LFP kinetic studies. These compounds have a long wavelength absorbance with λ_{max} at ca. 360 nm, and they are cleaved efficiently when irradiated with 355 nm light from a Nd:YAG laser. The first formed radicals are acyloxyl radicals (**5**) and the pyridine-2-thiyl radical (**4**) which absorbs strongly at 490 nm but relatively weakly in the region of 305−360 nm.[21] Alkylacyloxyl radicals decarboxylate with rate constants exceeding 10^8 s^{-1} at ambient temperatures, and the production of radicals **1** was "instant" on the nanosecond time scale. Following laser irradiation, signals from radicals **2** grew in smoothly with long wavelength absorbances at 330−335 nm as expected for diphenylalkyl radicals.[22] Figure 1 shows a time-resolved spectrum of product radical **2c** which is representative.

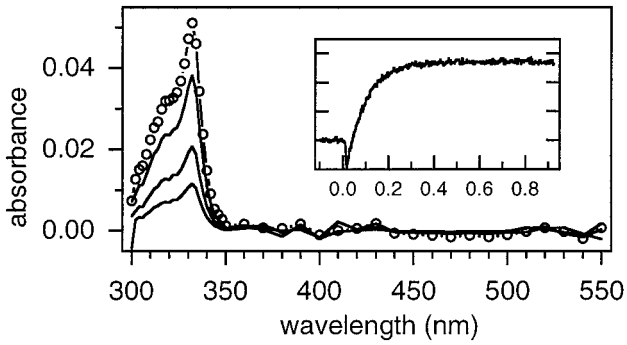


Figure 1. Time-resolved spectrum of radical **2c** in THF at 23 °C following laser irradiation of PTOC ester **3c**. The traces are at 61, 81, 141, and 261 ns after laser irradiation with the data at 41 ns subtracted to give a baseline. Symbols on the 261 ns trace show the wavelengths monitored. The inset shows the kinetic trace at 332 nm where the *x*-axis is time in microseconds.

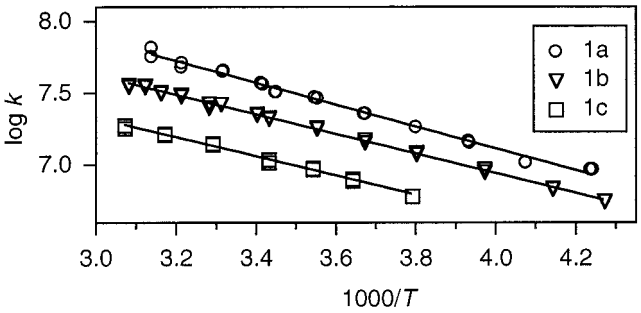


Figure 2. Observed rate constants for cyclizations of radicals **1** in THF. The lines are the Arrhenius functions listed in Table 1.

Rate constants for cyclizations of radicals **1** to **2** in THF were measured at various temperatures. An upper temperature limit of ca. 50 °C exists due to the thermal instability of the PTOC esters. Because dilute solutions of PTOC esters must be employed, lower temperature limits arise from the flow cell design. Radicals **1a** and **1b** were studied at temperatures as low as ca. −38 °C. The kinetic results are shown graphically in Figure 2, and tables containing the results are in the Supporting Information. For radical **1a**, the results are in good agreement with a rate constant previously reported at ambient temperature.[18] Each value of k_{obs} is an average of ca. 15 kinetic runs, and the errors in the observed rate constants were on the order of 2−5%. At the extreme temperatures, the differences in values of k_{obs} at temperatures that were nominally the same exceeded the error in k_{obs}, indicating that temperature control and measurement were the largest sources of error at the limits.

The observed rate constants were in the range of $(1-7) \times 10^7$ s^{-1}. Bimolecular radical−radical reactions and reactions of radicals with residual oxygen have pseudo-

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Table 1. Arrhenius Parameters for Cyclizations of Radicals 1 in THF[a]

radical	log A	E_a (kcal/mol)	k_{20} (s^{-1})[b]
1a	10.17 ± 0.11	3.49 ± 0.14	3.7×10^7
1b	9.67 ± 0.04	3.12 ± 0.05	2.2×10^7
1c	9.33 ± 0.10	3.06 ± 0.14	1.1×10^7

[a] Kinetic data is in Supporting Information. Errors at 2σ. [b] Rate constant at 20 °C.

first-order rate constants of $k < 1 \times 10^4$ s^{-1} and cannot introduce errors in the measured kinetics for such fast reactions. The largest measured rate constants, ca. 7×10^7 s^{-1} for cyclization of **1a** at 46 °C, were at the limit where convolution of the instrument response (measured as 2.5×10^8 s^{-1} for an instantaneous signal) begins to introduce a systematic error; specifically, an error of ca. 5% from instrument response convolution is expected for a reaction with $k = 6 \times 10^7$ s^{-1}.

The kinetic data for cyclizations of radicals **1** gives the Arrhenius parameters listed in Table 1 which also contains the calculated rate constants for the cyclizations at 20 °C. One probably would have anticipated that the rate constants for cyclization of radicals **1** would be in the order $k_{\mathbf{1a}} > k_{\mathbf{1b}} > k_{\mathbf{1c}}$, but the origin of this kinetic effect might be somewhat surprising. The activation energies *decrease* for the series **1a**, **1b**, **1c**, but increasingly unfavorable entropies of activation for the series, as reflected in the log A terms, more than offset the effects of the trend in activation energies.

The cyclizations of radicals **1** at ambient temperature are faster than those of the parent radicals (i.e. 5-hexenyl, etc.)[1] by slightly more than 2 orders of magnitude, a result consistent with the observation that at ambient temperature the methyl radical adds to 1,1-diphenylethene about 200 times faster than it adds to ethylene.[23] Similar results were found in comparing the rate constants for cyclization of 1-methoxy- and 1-ethoxycarbonyl-6,6-diphenyl-5-hexenyl radicals[24,25] with their nor-phenyl parent radicals.[26] Given the differences in character of the various radicals (electron-rich alkyl and α-methoxy versus electron-deficient α-ester), the major kinetic effect of the phenyl substitution apparently is a consistent reduction in $\Delta G^{\ddagger}$ related to the increased enthalpy of the reactions forming the diphenylalkyl radicals.

Calibration of Benzeneselenol Kinetics. Reactions of radicals **1** with PhSeH were studied by the PTOC-thiol indirect method (Scheme 2) that has previously been employed with a number of fast-reacting radicals.[1,13,17,27] In this method, PTOC esters are used as the radical precursors. Reactions of precursors **3** in radical chain propagation steps again give acyloxyl radicals **5** that decarboxylate to give radicals **1**. Radicals **1** either react with the trapping agent with rate constant k_T to give acyclic products **6** or cyclize to radicals **2** which will also react with the trapping agent, giving cyclic products **7**. The byproduct radical from the H-atom transfer steps, PhSe•, reacts with the PTOC ester at the thione group

Scheme 2

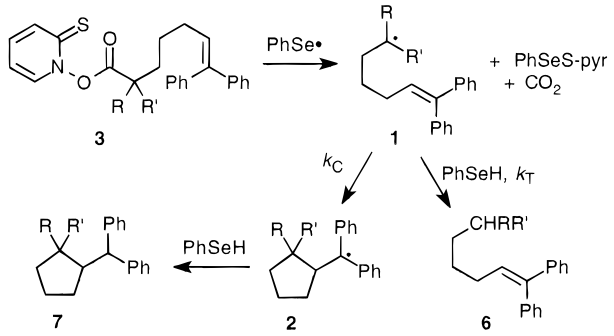

Table 2. Relative Arrhenius Parameters for Reactions of Radicals 1 with Group 16 Hydrides in THF

hydride	radical	log A	E_a (kcal/mol)
PhSeH	**1a**	0.56 ± 0.09	−1.27 ± 0.11
	1a[b]	0.55 ± 0.56	−1.24 ± 0.64
	1b	0.22 ± 0.18	−1.98 ± 0.22
	1c	0.64 ± 0.33	−1.90 ± 0.43
PhSH	**1a**[c]	−1.00 ± 0.23	−1.88 ± 0.30
t-BuSH	**1a**[c]	−2.02 ± 0.14	−1.63 ± 0.17

[a] Relative parameters for (k_T/k_C); data is in Supporting Information. Errors at 2σ. [b] Data from ref 28; benzene solvent. [c] Data from ref 18.

in another chain propagation step. This type of study is possible because of the high reactivity of the thione group of the PTOC esters with a number of radical types including sulfur- and selenium-centered radicals.[27]

A number of experimental precautions were taken due to the facile oxidation of PhSeH to diphenyl diselenide. Benzeneselenol was prepared by reaction of phenylmagnesium bromide with selenium. The product was distilled under nitrogen, sealed in ampoules under vacuum, and stored in the dark at ca. −60 °C. The content of each ampoule that was opened for kinetic studies was determined by GC to quantitate the extent of PhSeSePh contamination (which typically amounted to 3−5%), and the total concentration of PhSeH in the kinetic studies was adjusted for this contamination. Even with careful handling, the results of competition kinetic studies with nominal concentrations of PhSeH less than 0.04 M were not highly reproducible, and some reactions contained traces of radical oxidation products, e.g., (diphenylmethylene)cyclopentane from **1a**,[18] apparently from radical−radical disproportionation reactions. We assume that small amounts of residual oxygen in some reactions resulted in oxidation of PhSeH, and data from these studies was discarded. The kinetic data, provided in the Supporting Information, gave the relative Arrhenius parameters for trapping and cyclization (k_T/k_C) listed in Table 2.

The relative Arrhenius parameters for reaction of radical **1a** with PhSeH were previously reported by Crich et al.[28] The results of the present study conducted in THF solvent are indistinguishable from the results they found in benzene/toluene (see Table 2). In their study, PhSeH was produced by reaction of PhSeSePh with excess Bu_3SnH. The tin hydride also served as a sacrificial reductant for the PhSe• radical produced from reaction of PhSeH with the alkyl radical, and the chain reaction was carried by the Bu_3Sn• radical abstracting bromine atom

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Scheme 3

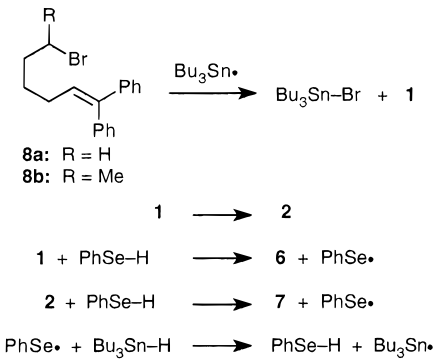

Table 3. Absolute Arrhenius Parameters for Reactions of Radicals with Group 16 Hydrides in THF[a]

hydride	radical	log *A*	E_a (kcal/mol)	k_{20} (M^{-1} s^{-1})[b]
PhSeH	**1a**	10.73 ± 0.14	2.22 ± 0.18	1.2×10^9
	1b	9.89 ± 0.18	1.14 ± 0.23	1.1×10^9
	1c	9.97 ± 0.34	1.16 ± 0.45	1.3×10^9
	CPC[c]	10.87 ± 0.14	2.10 ± 0.17	2.0×10^9
PhSH	**1a**	9.17 ± 0.26	1.61 ± 0.39	9×10^7
t-BuSH	**1a**	8.15 ± 0.18	1.86 ± 0.23	6×10^6

[a] Calculated from the data in Tables 1 and 2 unless noted. Errors are 2σ. [b] Rate constant for reaction at 20 °C. [c] Cyclopropylcarbinyl radical; data from ref 17.

from the alkyl bromide precursor **8a** (Scheme 3).[28] The relatively large errors in the parameters determined by Crich et al. resulted from limited data, but when several concentrations of PhSeH were employed at 20 °C, they found $k_T/k_C = 29$ M^{-1}, which is in good agreement with the value $k_T/k_C = 32$ M^{-1} found in this work.

For an independent check on the kinetics of PhSeH trapping, we employed Crich's method[28] with radicals **1a** and **1b** using the appropriate bromide precursors **8a** and **8b**. The relative kinetic expressions for trapping and cyclization of **1a** were $k_T/k_C = (26 \pm 1)$ M^{-1} in benzene at 34 °C and $k_T/k_C = (25 \pm 2)$ M^{-1} in toluene at 33 °C. These values compare favorably with $k_T/k_C = 29$ M^{-1} at these temperatures calculated from the parameters in Table 2 for reaction of **1a** in THF. For radical **1b** at 34 °C in benzene, we obtained $k_T/k_C = (40 \pm 2)$ M^{-1} which can be compared to $k_T/k_C = 43$ M^{-1} calculated from the parameters in Table 2 for reaction of **1b** in THF.

Solvent effects on the kinetics of cyclizations of radicals **1** are likely to be quite small,[3-5] and the agreement between the ratios of rate constants determined in THF and those obtained in aromatic solvents suggests that rate constants for reactions of PhSeH with alkyl radicals are also relatively insensitive to solvent polarity. Perhaps more importantly, the agreement in values from the two different methods suggests that the relative rate constants are reasonably accurate in the vicinity of ambient temperature.

Relative rate constants for reactions of radical **1a** with *t*-BuSH and with PhSH were previously reported.[18] For discussion below, we have included the relative Arrhenius parameters for these reactions in Table 2.

Adjusting the Alkyl Radical Kinetic Scale. Combination of the Arrhenius parameters for trapping versus cyclization listed in Table 2 with the absolute Arrhenius parameters for the cyclization reactions in Table 1 gives the absolute Arrhenius parameters for the bimolecular H-atom transfer reactions that are listed in Table 3. Included in Table 3 are the absolute Arrhenius parameters reported for reaction of PhSeH with the cyclopropylcarbinyl radical.[17] The rate constants at 20 °C for reactions of the Group 16 hydrides with the various radicals calculated from these parameters are also listed.[29]

One point that should be noted at the outset is that the Arrhenius parameters for reactions of PhSeH must be considered operational values. That is, these parameters might accurately predict rate constants for the H-atom transfer reactions but they are unlikely to give correct values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ because the reactions are partially diffusion-controlled. Diffusional rate constants for thiophenol in THF determined by the pulse-gradient spin−echo NMR technique fit the equation $\log(k_{diff}/M^{-1}s^{-1}) = 12.14 - 2.54/2.3RT$,[30] and this equation should be reasonably accurate for predicting the diffusional rate constants for PhSeH. Accordingly, the expected diffusional rate constants for PhSeH are about a factor of 15 larger than the observed rate constants for reactions of PhSeH at 20 °C. The effect of partial diffusion control is to give observed rate constants that are slightly less than the chemical rate constants (7% at 20 °C). However, the E_a term in the apparent Arrhenius function for diffusion is larger than those expected for the H-atom trapping reactions, and diffusional effects become increasingly important at lower temperatures. The result is that a plot of $\log(k_{obs})$ versus $1/T$ should describe a slight curve, and a linear solution to the curved data will give log *A* and E_a terms that are too large.

Another caution regarding the Arrhenius parameters for PhSeH reactions listed in Table 3 is in order. The precisions are relatively good, but one should be concerned that systematic errors might be hidden by the precision. Rate constants at the lower temperatures should be more suspect. The relative rate constants for trapping and rearrangement of radicals **1** (k_T/k_C) ranged from about 25 M^{-1} at 40 °C to 60−160 M^{-1} at −40 °C. Rate constants calculated from these functions in the vicinity of ambient temperature are inherently more likely to be accurate than those for lower temperatures, and there is good agreement for the relative rate constants for **1a** and **1b** determined by two methods in the range of 30−35 °C.

The rate constants for reaction of PhSeH with the primary alkyl radical **1a** are smaller than those previ-

(29) A referee requested that we comment on error propagation for the Arrhenius functions for PhSeH trapping; this was conventional (i.e. square root of the sum of the squares), and the errors in the absolute Arrhenius functions derive mainly from the relative Arrhenius functions. An understanding of the precision and accuracy of the kinetic values determined in this work is more important. The precision in determining the first-order rate constants is excellent with errors of only a few percent in most cases. The accuracy of first-order rate constants in the 10^6-10^7 s^{-1} range is also expected to be very good because systematic errors in the apparatus and experimental design are minimal in this range (see text). The precision in the indirect kinetic determinations is poorer, with standard deviations in relative rate constants at a given temperature as large as 15% but more typically 5% or less. The Arrhenius functions for PhSeH trapping reproduce the kinetics of trapping within the temperature ranges studied with deviations from the experimental average values that are typically 1−5% but range up to 12%. The errors in the Arrhenius functions for the cyclizations of radicals **1** belie the precision in the kinetic values and result largely from the somewhat limited temperature ranges studied; meaningful information about the enthalpies and entropies of activation are contained in these values. We emphasize that the Arrhenius functions for reactions of PhSeH are only operational due to partial diffusion control conditions (see text), and these values should not be used for calculating activation parameters; the true activation energies for H-atom transfer from PhSeH almost certainly are smaller than those from PhSH.

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ously found when PhSeH was calibrated indirectly against the cyclopropylcarbinyl radical ring opening.[13,17] Given the near equalities of the rate constants for PhSeH reactions with the 1°, 2°, and 3° radicals **1a**−**c** at 20 °C, we believe this discrepancy is unlikely to be due to differences in the reactivities of the two radicals. Specifically, we believe that the cyclopropylcarbinyl radical ring opening values used to calibrate PhSeH were in error, and we develop this point below.

The Arrhenius parameters for *t*-BuSH reactions with radical **1a** are in reasonably good agreement with the values previously determined for reactions of this thiol with primary alkyl radicals by a series of indirect kinetic studies.[31] For example, the rate constant for *t*-BuSH reaction with radical **1a** at 20 °C of 6×10^6 M^{-1} s^{-1} is slightly smaller than the value of 7.5×10^6 M^{-1} s^{-1} obtained in the earlier work.[31] We recommend the use of the Arrhenius function in Table 3 for predicting the rate constants for reactions of primary alkyl radicals with *t*-BuSH.

The Arrhenius parameters for reactions of PhSH with radical **1a** in Table 3 can be compared to values for reactions of PhSH with primary alkyl radicals determined by LFP methods.[8] In the original LFP study, rate constants for reactions of PhSH with the butyl radical and the octyl radical at 20 °C differed by about 35%. The rate constants calculated from the Arrhenius function in Table 3 are in good agreement with the LFP rate constants for reaction of the octyl radical and smaller than those determined for reaction of the butyl radical.[8] The rate constants for reaction of PhSH with the butyl radical were given in a review of alkyl radical kinetics,[1] but we suggest that the values for reaction of PhSH with the octyl radical[8] and radical **1a** are likely to be more accurate as representative rate constants for reactions of PhSH with primary alkyl radicals.

The selection of the kinetics of butyl radical reactions with PhSH as the appropriate set of rate constants for reactions of primary alkyl radicals with this thiol apparently resulted in the discrepancy between the rate constants for reaction of PhSeH with the cyclopropylcarbinyl radical and radicals **1**. In the vicinity of ambient temperatures, our group calibrated the cyclopropylcarbinyl radical via the PTOC-thiol method using PhSH trapping, and we used the rate constants for PhSH reported for reactions of the butyl radical.[27] Accordingly, the rate constants for cyclopropylcarbinyl radical ring opening we determined might be too large by up to 35%, and these values for cyclopropylcarbinyl radical ring opening were used for the PhSeH calibrations.[17] If we adjust the rate constants for cyclopropylcarbinyl radical ring opening by using the values for PhSH reactions with **1a** instead of the values for reaction of PhSH with the butyl radical, the rate constants for reactions of PhSeH with the cyclopropylcarbinyl radical will be indistinguishable from those for reaction of PhSeH with **1a**.

On the basis of the above, we suggest that the kinetic values for PhSeH trapping of radical **1a** calculated from the Arrhenius function in Table 3 are more likely to be accurate than the reported values for PhSeH reactions with the cyclopropylcarbinyl radical, and we recommend that the Arrhenius parameters for reactions of PhSeH with **1a** be applied for the calibrations of the very fast ring opening reactions of aryl-substituted cyclopropylcarbinyl radicals.[14−16] Such a change in the values of the PhSeH rate constants will result in a decrease in the previously published rate constants for ring openings of 2-aryl-substituted cyclopropylcarbinyl radicals by about 35%.

The cyclopropylcarbinyl radical ring opening is one of the more securely calibrated radical reactions, and one should exercise caution in recommending changes in the rate constants for this reaction. Fortunately, a shift in the values for the rate constants for cyclopropylcarbinyl ring opening determined by the PTOC-thiol method with PhSH trapping[27] will have only a minor affect on the Arrhenius parameters for ring opening of this radical. A commonly employed Arrhenius function for cyclopropylcarbinyl radical ring opening was determined[27] from three sets of data over a wide temperature range and is largely controlled by low-temperature ESR studies[32] and high-temperature nitroxyl radical trapping results.[11] For equally weighted data, changing the values for cyclopropylcarbinyl ring opening determined against PhSH trapping will lead to a reduction in the log *A* term by 0.10 and a reduction in E_a by 0.06 kcal/mol and will slightly improve the precision in both terms. The net result will be a reduction in the calculated rate constant at 20 °C for the cyclopropylcarbinyl radical ring opening by about 13%. The modified Arrhenius function for cyclopropylcarbinyl ring opening using equal weighting for the data from the three studies[11,27,32] is $\log(k/s^{-1}) = (13.04_5 \pm 0.10) - (6.99 \pm 0.09)/\theta$ (kcal/mol, errors at 2σ) giving a rate constant at 20 °C of 6.7×10^7 s^{-1}.

We believe the new values for cyclopropylcarbinyl radical ring opening are likely to be more accurate than those previously reported, and we recommend their use. The rate constants and Arrhenius parameters for cyclopropylcarbinyl radical ring openings obtained a decade ago[27] have been used in calibrations of several radical reactions, and one should note that the recommended change will have an effect on the kinetics of other radical reactions that depends on how the values were used. A comparison involving competition against the cyclopropylcarbinyl radical ring opening obviously will change by the same percentage as the ring opening kinetics change. However, the kinetics of a number of substituted cyclopropylcarbinyl radical ring openings were determined by measuring one rate constant and employing the value of log *A* for the cyclopropylcarbinyl radical,[33] and the small change in the log *A* value will have little effect on the calculated kinetics for these radicals unless the results are extrapolated far from ambient temperature.

Conclusion

The rate constants for cyclizations of radicals **1** measured directly by LFP provide a relatively precise set of data at the upper end of the alkyl radical kinetic scale and are useful as primary kinetic standards for fast alkyl radical reactions. Second-order rate constants for reactions of these radicals with PhSeH have good precision, and the rate constants for reactions of PhSeH with the primary alkyl radical **1a** appear to be more reliable than those determined against cyclopropylcarbinyl radical ring

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opening due to a systematic error in the latter values. The new values for reactions of PhSeH with primary alkyl radicals suggest that previous radical rate constants at ambient temperature determined by competition against PhSeH trapping should be reduced by about 35%.

Experimental Section

General Methods. Commercially available reagents were purchased from Aldrich Chemical Co. unless otherwise noted. All moisture-sensitive reactions were performed in a flame-dried glassware under an atmosphere of nitrogen. Tetrahydrofuran (THF) and ether were freshly distilled from sodium benzophenone ketyl under nitrogen immediately before use. Methylene chloride was distilled under a nitrogen atmosphere from phosphorus pentoxide. Benzene was distilled over calcium hydride under nitrogen. Dimethyl formamide (DMF) was distilled from calcium hydride. *N*-Hydroxypyridine-2-thione sodium salt was prepared as described previously.[34]

^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were obtained at 300 or 500 MHz and 75 or 125 MHz, respectively. Gas chromatography analyses were performed using flame ionization detectors on 15 m × 0.54 mm bonded phase SE-30 and Carbowax columns. GC-mass spectrometry was accomplished with a Hewlett-Packard Model 5791 mass selective detector interfaced to a Hewlett-Packard Model 5890 series II gas chromatograph; a 30 m × 0.25 mm capillary bonded phase Carbowax column was employed. High-resolution mass spectral analyses were performed by the Central Instrumentation Facility at Wayne State University. Melting points are uncorrected. Radial chromatography was performed on plates coated with 2 mm of TLC grade silica gel with gypsum binder and fluorescent indicator.

General Procedure for Preparation of PTOC Esters 3a−c. To a solution of the appropriate acid (1.0 equiv) in dry benzene at 0 °C under nitrogen was added dropwise oxalyl chloride (2.5 equiv) via syringe followed by two drops of DMF. The reaction mixture was stirred for 4−5 h at room temperature until gas evolution ceased. The excess oxalyl chloride and benzene were removed under reduced pressure. The resulting acid chloride was dissolved in dry benzene and transferred by cannula into a light-shielded flask in an ice bath containing a suspension of *N*-hydroxypyridine-2-thione sodium salt (1.1 equiv) and a catalytic amount of DMAP (5 mol %) in dry benzene. The mixture was allowed to warm to room temperature with stirring and was maintained at room temperature for 3 h. The mixture was diluted with ether and washed with a saturated $NaHCO_3$ solution and a saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated to give the crude PTOC ester which was purified by column chromatography on silica gel or by recrystallization.

7,7-Diphenyl-6-heptenoic acid 2-thioxo-*2H*-pyridin-1-yl ester (**3a**) was prepared as previously described.[18]

7,7-Diphenyl-2-methyl-6-heptenoic acid was obtained by hydrolysis of ethyl 7,7-diphenyl-2-methyl-2-(ethoxycarbonyl)-6-heptenoate[25] followed by thermal decarboxylation of the malonic acid. A solution of the diester[25] (3.0 g, 7.63 mmol) and KOH (0.86 g, 19.1 mmol, 2.5 equiv) in 60 mL of 95% ethanol was heated at reflux for 5 h. The mixture was cooled to room temperature and concentrated at reduced pressure. The residue was dissolved in water (30 mL), and the mixture was extracted with ether (5 mL) to remove organic impurities. The basic aqueous layer was acidified to pH 2−3 with a 1 M HCl solution, and the resulting solution was extracted with ether (3 × 20 mL). The organic layer was washed with a saturated solution of brine, dried over $MgSO_4$, and concentrated to give the crude product. A flask containing 2.6 g of diacid was equipped with a bubbler and heated at 170 °C in an oil bath until the evolution of CO_2 ceased (ca. 3 h). The desired product was purified by column chromatography on silica gel (hexanes:EtOAc; 1:1) to yield 2.0 g (6.80 mmol, 89%) of a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.18 (3H, d, J = 7.2 Hz), 1.45−1.54 (3H, m), 1.71 (1H, m), 2.14 (2H, q, J = 7.2 Hz), 2.44 (1H, m), 6.08 (1H, t, J = 7.5 Hz), 7.16−7.41 (10H, m) 11.5−11.9 (1H, bs). ^{13}C NMR ($CDCl_3$): δ 16.8, 27.4, 29.5, 33.0, 39.2, 126.8, 126.9, 127.2, 128.0, 128.1, 129.3, 129.8, 140.1, 142.0, 142.7, 183.2. MS: *m*/*z* (rel intens), 91 (45.8), 115 (68.3), 165 (20.3), 167 (25.5), 178 (22.5), 193 (100.0), 294 (30.4). HRMS: calcd for $C_{20}H_{22}O_2$, 294.1619; found, 294.1618.

7,7-Diphenyl-2-methyl-6-heptenoic acid 2-thioxo-*2H*-pyridin-1-yl ester (**3b**) was prepared from 1.0 g (3.4 mmol) of the above acid by the general method. Column chromatography (hexanes:EtOAc; 6:4) on silica gel gave 1.1 g of PTOC ester **3b** (2.73 mmol, 80%). ^{1}H NMR ($CDCl_3$): δ 1.38 (3H, d, J = 6.9 Hz), 1.50−1.66 (3H, m), 1.91 (1H, m), 2.17 (2H, q, J = 7.2 Hz), 2.82 (1H, m), 6.09 (1H, t, J = 7.2 Hz), 6.60 (1H, dt, J = 1.8, 6.9 Hz), 7.16−7.41 (11H, m), 7.46 (1H, dt, J = 1.5, 6.9 Hz), 7.69 (1H, dt, J = 1.8, 9.0 Hz). ^{13}C NMR ($CDCl_3$): δ 16.8, 27.3, 29.4, 32.8, 37.4, 112.4, 126.8, 126.9, 127.2, 128.0, 128.2, 129.0, 129.8, 133.3, 137.5, 137.6, 140.0, 142.2, 142.5, 171.9, 175.9.

7,7-Diphenyl-2,2-dimethyl-6-heptenoic acid was prepared by the reaction of 5-bromo-1,1-diphenyl-1-pentene with the enolate prepared by reaction of isobutyric acid and LDA. To a flame-dried flask under nitrogen equipped with a stir bar was added 2.16 g (21.3 mmol, 2.2 equiv) of freshly distilled diisopropylamine and 20 mL of anhydrous THF. The solution was cooled to 0 °C, and 21.3 mmol of *n*-BuLi (8.54 mL of a 2.5 M solution in hexanes) was added via syringe. The resulting solution was stirred at 0 °C for 0.5 h and then cooled to −78 °C. A solution of 0.854 g (9.7 mmol) of isobutyric acid in 5 mL of THF was slowly added to the reaction flask by cannula. After allowing the reaction to warm to 20 °C for 0.5 h followed by the addition of DMPU (5 mL), the reaction mixture was cooled to −50 °C. A solution of 2.9 g (9.7 mmol) of 5-bromo-1,1-diphenyl-1-pentene in 5 mL of THF was added to the flask by cannula. The reaction was allowed to warm to room temperature and to stand overnight. The mixture was dissolved in water (50 mL), and the resulting mixture was extracted with ether (3 × 5 mL) to remove organic impurities. The basic aqueous solution was acidified (HCl) and extracted with ether (3 × 25 mL). The combined organic phase was dried over $MgSO_4$ and concentrated. The crude product was purified by recrystallization from hexanes:ethanol to yield 2.0 g (6.5 mmol, 67%) of the desired acid as colorless crystals. Mp: 109−109.5 °C. ^{1}H NMR ($CDCl_3$): δ 1.19 (6H, s), 1.40−1.48 (2H, m), 1.53−1.56 (2H, m), 2.11 (2H, q, J = 7.0 Hz), 6.06 (1H, t, J = 7.5 Hz), 7.14−7.38 (10H, m), 11.6−11.9 (1H, bs). ^{13}C NMR ($CDCl_3$): δ 24.9, 25.3, 30.1, 40.0, 42.1, 126.8, 126.9, 127.2, 128.0, 128.1, 129.5, 129.9, 140.1, 141.8, 142.7, 184.6. MS: *m*/*z* (rel intens), 91 (36.8), 115 (63.7), 178 (24.6), 180 (33.5), 193 (100.0), 206 (23.5), 308 (24.5). HRMS: calcd for $C_{21}H_{24}O_2$, 308.1776; found, 308.1780.

7,7-Diphenyl-2,2-dimethyl-6-heptenoic acid 2-thioxo-*2H*-pyridin-1-yl ester (**3c**) was prepared from 0.4 g (1.3 mmol) of the above acid by the general method. The crude residue was purified by recrystallization from hexanes:ether to give 0.45 g (1.08 mmol, 83%) of PTOC ester **3c** as bright yellow crystals. ^{1}H NMR ($CDCl_3$): δ 1.42 (6H, s), 1.53−1.60 (2H, m), 1.74 (2H, m), 2.16 (2H, q, J = 7.5 Hz), 6.09 (1H, t, J = 7.5 Hz), 6.59 (1H, dt, J = 1.5, 6.5 Hz), 7.15−7.40 (12H, m), 7.67 (1H, d, J = 9.0 Hz). ^{13}C NMR ($CDCl_3$): δ 25.0, 25.2, 29.9, 39.9, 42.4, 112.5, 126.8, 126.9, 127.2, 128.0, 128.2, 129.1, 129.8, 133.3, 137.5, 137.6, 140.0, 142.2, 142.5, 171.9, 175.9.

1,1-Diphenyl-1-hexene (**6a**) was prepared as previously described.[18]

1,1-Diphenyl-1-heptene (**6b**). To a light-protected solution of 100 mg (0.25 mmol) of PTOC ester **3b** in 10 mL of dry, degassed THF under nitrogen with a stir bar was added 393 mg (10 equiv, 265 μL, 2.5 mmol) of PhSeH via syringe. The shield was removed, and the reaction mixture was irradiated at room temperature with a 150 W tungsten-filament lamp at a distance of 0.5 m for 2 h. The solvent was removed at reduced pressure. Column chromatography of the crude products on silica gel (2% EtOAc in hexanes, R_f = 0.8) gave 37 mg (0.15 mmol, 60%) of desired product **6b** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.89 (3H, t, J = 7.1 Hz), 1.29 (4H, m), 1.47

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(2H, m), 2.14 (2H, q, J = 7.5 Hz), 6.12 (1H, t, J = 7.8 Hz), 7.19−7.42 (10H, m). ^{13}C NMR ($CDCl_3$): δ 14.0, 22.5, 29.6, 29.7, 31.5, 126.7, 126.8, 127.2, 128.0, 128.1, 129.9, 130.3, 140.3, 141.4, 142.9. MS: *m*/*z* (rel intens), 91 (37.3), 115 (67.0), 165 (20.1), 178 (25.3), 180 (34.6), 193 (100.0), 250 (40.7). HRMS: calcd for $C_{19}H_{22}$, 250.1722; found, 250.1722.

1,1-Diphenyl-6-methyl-1-heptene (**6c**). To a light-protected solution of crude PTOC ester **3c** (140 mg, 0.34 mmol) in 20 mL of dry, degassed benzene under nitrogen with a stir bar was added 534 mg (10 equiv, 361 μL, 3.4 mmol) of PhSeH via syringe. The shield was removed, and the reaction mixture was irradiated at room temperature with a 150 W tungsten-filament lamp at a distance of 0.5 m for 3 h. The mixture was diluted with ether and washed with a 10% $NaHCO_3$ solution and a saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated. Column chromatography of the residue on silica gel (2% EtOAc in hexanes, R_f = 0.8) gave 45 mg (0.17 mmol, 50%) of desired product **6c** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.89 (6H, d, J = 6.6 Hz), 1.20 (2H, m), 1.41−1.56 (3H, m), 2.11 (2H, q, J = 7.5 Hz), 6.12 (1H, t, J = 7.2 Hz), 7.19−7.40 (10H, m). ^{13}C NMR ($CDCl_3$): δ 22.6, 27.7, 27.8, 30.0, 38.6, 126.7, 126.8, 127.2, 128.0, 128.1, 129.9, 130.3, 140.3, 141.4, 142.9. MS: *m*/*z* (rel intens), 91 (32.6), 115 (66.8), 165 (29.6), 178 (33.5), 180 (58.6), 192 (32.2), 193 (100.0), 264 (50.6). HRMS: calcd for $C_{20}H_{24}$, 264.1878; found, 264.1869.

(Diphenylmethyl)cyclopentane (**7a**) was prepared as previously described.[18]

2-(Diphenylmethyl)-1-methylcyclopentane (**7b**) was isolated from a reaction of crude PTOC ester **3b** and Bu_3SnH. PTOC ester **3b** was prepared as above from 140 mg (0.48 mmol) of the acid. To the benzene solution of the crude PTOC ester was added 273 mg (0.94 mmol) of Bu_3SnH. The reaction mixture was irradiated with a 150 W tungsten-filament lamp for 3 h. The mixture was diluted with ether and washed with a 10% $NaHCO_3$ solution and a saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated. Purification of the residue by column chromatography on silica gel (hexanes/EtOAc, 9:1, R_f = 0.7) gave 70 mg (0.28 mmol, 58%) of a 4:1 mixture of diastereomers of **7b**. Spectra for the major diastereomer follow. ^{1}H NMR ($CDCl_3$): δ 0.74 (3H, d, J = 6.9 Hz), 1.22−1.65 (6H, m), 2.06 (1H, q, J = 7.2 Hz), 2.73 (1H, m), 3.70 (1H, d, J = 12 Hz), 7.12−7.40 (10H, m). ^{13}C NMR ($CDCl_3$): δ 14.5, 22.0, 28.4, 33.7, 34.5, 47.8, 54.1, 125.8, 125.9, 127.7, 127.9, 128.2, 128.3, 144.7, 145.8. MS: *m*/*z* (rel intens), 83 (23.6), 165 (22.6), 167 (100.0), 168 (52.4), 250 (7.0). HRMS: calcd for $C_{19}H_{22}$, 250.1722; found, 250.1722.

2-(Diphenylmethyl)-1,1-dimethylcyclopentane (**7c**) was prepared by the method used for preparation of **7b** from crude PTOC ester **3c** (140 mg, 0.34 mmol). Column chromatography of the crude products on silica gel (hexanes/EtOAc; 9:1, R_f = 0.7) gave 35 mg (0.13 mmol, 38%) of **7c** as an oil. ^{1}H NMR ($CDCl_3$): δ 0.49 (3H, s), 0.90 (3H, s), 1.28 (1H, m), 1.39−1.53 (4H, m), 1.65 (1H, m), 2.50 (1H, m), 3.67 (1H, d, J = 11.7 Hz), 7.07−7.38 (10H, m). ^{13}C NMR ($CDCl_3$): δ 20.4, 21.8, 29.6, 31.9, 41.1, 44.2, 51.9, 55.3, 125.8, 126.0, 127.8, 128.2, 128.3, 128.33, 145.1, 146.1. MS: *m*/*z* (rel intens), 55 (73.7), 67 (29.1), 81 (25.7), 96 (96.1), 97 (91.5), 165 (34.6), 166(19.7), 167 (100.0), 168 (57.5), 264 (7.0). HRMS: calcd for $C_{20}H_{24}$, 264.1878; found, 264.1872.

(Diphenylmethylene)cyclopentane was prepared from the reaction of cyclopentanecarbonyl chloride (2.0 g, 15.1 mmol) and phenylmagnesium bromide (40 mmol) in 15 mL of ether under nitrogen followed by dehydration of the intermediate alcohol with *p*-toluenesulfonic acid (benzene, reflux, 10 h). A standard workup followed by column chromatography on silica gel (hexanes/EtOAc; 9:1) gave the desired product (2.1 g, 61%). The ^{1}H NMR spectrum was consistent with that reported.[35] ^{13}C NMR ($CDCl_3$): δ 26.8, 33.2, 126.0, 127.9, 129.2, 143.5.

6-Bromo-1,1-diphenyl-1-heptene (**8b**). 6,6-Diphenyl-5-hexenoic acid was converted to the acid chloride which was allowed to react with *N*,*O*-dimethylhydroxyamine to give the Weinreb amide which was allowed to react with MeMgBr to give 7,7-diphenyl-6-hepten-2-one. Reduction of the ketone with $NaBH_4$ in 20 mL of EtOH gave the corresponding alcohol which was converted to the mesylate by reaction with excess MsCl in pyridine. Bromide **8b** was prepared by reaction of the mesylate with LiBr in refluxing acetone; the crude product was purified by chromatography on silica gel (hexanes/EtOAc; 95/5) to give the desired product as an oil in 62% yield from the ketone. ^{1}H NMR ($CDCl_3$): δ 1.58−1.68 (1H, m), 1.74 (3H, d, J = 6.8 Hz), 1.80−1.92 (3H, m), 2.16−2.24 (2H, m), 4.08−4.17 (1H, m), 6.14 (1H, t, J = 7.2 Hz), 7.22−7.46 (10H, m). ^{13}C NMR ($CDCl_3$): δ 26.4, 28.0, 28.9, 40.5, 51.5, 126.8, 126.9, 127.2, 128.1, 128.2, 128.4, 129.2, 129.8, 140.0, 142.1, 142.5. Ms: *m*/*z* (rel intens), 91 (29), 115 (49), 178 (21), 193 (100), 328 (23), 330 (23). HRMS: calcd for $C_{19}H_{21}{}^{79}Br$, 328.0827; found, 328.0821.

Indirect kinetic studies followed the method of Newcomb et al. previously described.[14,17,18] Benzeneselenol, prepared by the method of Foster,[36] was distilled under subdued light. In a flame-dried tube shielded from light containing a small stir bar, a mixture of radical precursors (0.02−0.04 M), PhSeH (0.06−0.3 M), and a hydrocarbon standard (pentadecane) in freshly distilled THF was sparged with nitrogen. The tubes were equilibrated in a temperature-regulated bath for several minutes. The shields were removed, and the stirring mixture was irradiated with a 150 W tungsten filament lamp placed 0.4 m from the tube. After 40 min, the tubes were cooled at −78 °C, and the reaction mixture was analyzed by GC. All yields reported for indirect kinetic experiments were calculated from response factors determined with authentic samples. Results are provided in the Supporting Information.

Direct kinetic studies were performed as described previously.[5] Kinetic results are provided in the Supporting Information.

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Supporting Information Available: Tables of kinetic data for cyclizations of radicals **1** and competitition kinetic results and ^{1}H and ^{13}C NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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