Radical Clock Reactions under Pseudo-First-Order Conditions Using Catalytic Quantities of Diphenyl Diselenide. A ^{77}Se- and ^{119}Sn-NMR Study of the Reaction of Tributylstannane and Diphenyl Diselenide

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A method for the trapping of alkyl radicals by constant, catalytic quantities of PhSeH as a clock reaction in radical kinetics is presented. PhSeH is introduced in the form of PhSeSePh and regenerated by slow addition of a stoichiometric quantity of Bu_3SnH. Using this method the rate constant for cyclization of the 6,6-diphenyl-5-hexenyl radical was found to be 6.8×10^7 s^{-1} at 20 °C, in fair agreement with the literature value of 4×10^7 s^{-1}. An extension of the method was used to determine the rate of quenching of the 2,3,4,6-tetra-*O*-acetoxy-1-glucosyl radical by PhSeH as 3.6×10^6 s^{-1} at 78 °C. The reaction of Bu_3SnH and PhSePh was studied by a combination of ^{77}Se- and ^{119}Sn-NMR spectroscopy.

Introduction

The very considerable success[1] seen in recent years in the application of free radical chain reactions, of ever increasing complexity, is underpinned by the painstaking work of physical organic chemists involved in establishing a data base of rate constants[2] for individual radical reaction steps. Appreciation of this data base is invaluable as it enables synthetic chemists to predict with some confidence whether a particular chain sequence will provide the desired product or not. The most common approach for the determination of a radical rate constant involves the use of a calibrated radical clock whereby the reaction under investigation is pitted against a rearrangement of known rate in a competition reaction. The desired rate is then obtained from the ratio of products formed. When the competition is intermolecular it is usual to use one of the reagents in large excess such that pseudo-first-order kinetics may be assumed and the experiment and calculations considerably simplified. Alternatively, in order to make the same assumption, the reaction is only run to low conversion. This approach has been widely and successfully applied but problems can arise through the necessity of determining ratios of products accurately in the presence of a large excess of reagent or of substrate depending on which protocol is employed. Much of the work in the literature has relied on the use of the abstraction of hydrogen atoms from Bu_3SnH by primary alkyl radicals ($k_{25} = 2.4 \times 10^6$ M^{-1} s^{-1})[3] as a clock reaction, but the need for faster clock reactions in the determination of picosecond radical kinetics has prompted Newcomb to introduce the use of hydrogen atom abstraction from PhSeH ($k_{25} = 2.1 \times 10^9$ M^{-1} s^{-1} for a primary alkyl radical).[4] Here, we introduce a new method for the use of the PhSeH radical clock which operates under pseudo-first-order conditions, without an excess of reagent, and in which reactions are run to completion. Problems due to analysis of small quantities of product in the presence of excess reagent or substrate are therefore avoided. Furthermore, PhSeH is introduced in a catalytic quantity in the form of PhSeSePh which obviates the need to prepare and manipulate this highly air sensitive, noxious compound.

Results and Discussion

Recently, we described the catalysis of Bu_3SnH reductions of alkyl halides by catalytic quantities of PhSeH, introduced as PhSeSePh, and its application to the prevention of unwanted radical rearrangments.[5] Key steps in this chemistry are the rapid reduction of PhSeSePh by Bu_3SnH (eq 1).

$$R_3SnH + PhSeSePh \rightarrow R_3SnSePh + PhSeH \quad (1)$$

and the three propagation step chain sequence (eqs 2−4).

$$Bu_3Sn^\bullet + RX \rightarrow Bu_3SnX + R^\bullet \quad (2)$$

$$R^\bullet + PhSeH \rightarrow RH + PhSe^\bullet \quad (3)$$

$$PhSe^\bullet + Bu_3SnH \rightarrow PhSeH + Bu_3Sn^\bullet \quad (4)$$

This sequence, which enabled us to take advantage of the very superior properties of PhSeH as a trap for nucleophilic alkyl radicals, can be thought of as an example of polarity reversal catalysis as enunciated by Roberts.[6,7] Thus, the abstraction of a hydrogen atom from Bu_3SnH by a nucleophilic alkyl radical is unfavorable due to the hydridic nature of the tin hydride,

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[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

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[2] (a) Lanholt-Bornstein New Series, Vol. 13abc, Fischer, H., Ed., Springer Verlag: Berlin, 1983, 1984, 1985. (b) Ingold, K. U.; Griller, D. *Acc. Chem. Res.* **1980**, *13*, 317. (c) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

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

[4] (a) Newcomb, M.; Varick, T. R.; Ha, C.; Manek, M. B.; Yue, X. *J. Am. Chem. Soc.* **1992**, *114*, 8158. (b) Martin-Esker, A. A.; Johnson, C. C.; Horner, J. H.; Newcomb, M. *J. Am. Chem. Soc.* **1994**, *116*, 9174.

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0022-3263/96/1961-2368$12.00/0

whereas that from PhSeH is favorable due to its acidic nature. The cycle is completed (eq 4) when the electrophilic PhSe• radical abstracts the electron rich hydrogen from the stannane, a reaction in which the polarities are nicely matched.[8]

We reasoned that, by application of the above catalytic cycle, the PhSeH clock[4] could be applied to the measurement of a wide range of radical kinetics. The clock sequence to be applied mirrors closely that in Newcomb's excellent work; however, the PhSeH is used in substoichiometric quantities, rather than in excess, and is regenerated by slow addition of Bu_3SnH. Consider the general case for determination of the rate constant for the rearrangement of a radical A• to a radical B•. Dropwise addition of *1 mol equiv* of Bu_3SnH to a mixture of radical precursor A−X, wherein X is Br, I, or PhSe and a precisely controlled catalytic amount of PhSeH will result in the formation of the reduction product A−H and the rearranged product B−H. The thousandfold difference in rates for the quenching of A• (and B•) by PhSeH and Bu_3SnH, coupled with the rapid recycling of PhSeH and the dropwise addition of Bu_3SnH, renders the contribution of Bu_3SnH to the trapping of A• negligible and ensures that the concentration of PhSeH is kept constant. The conditions for pseudo-first-order kinetics are therefore established. Moreover, it should be possible to run the reaction to complete consumption of A−X, without the need for an excess of PhSeH or Bu_3SnH: the analytical problems alluded to above are therefore avoided. Conducting several runs in the presence of different concentrations of PhSeH will enable a linear plot of A−H/B−H against [PhSeH] to be traced for which the slope is the ratio of k_H/k_R where k_R is the rate of the rearrangement and k_H the known rate of quenching of A• by PhSeH (Scheme 1). In this manner it should be possible to determine the rates of a wide variety of radical rearrangements. Alternatively, using a rearrangement of known rate, it should be possible to determine the rate of hydrogen abstraction from PhSeH by a variety of differently substituted alkyl radicals.

Scheme 1

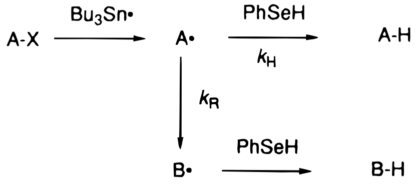

Table 1. Relevant ^{77}Se-NMR Chemical Shifts

compound	δ (C_6D_6)
PhSeSePh	460
$Bu_3SnSePh$	−27.7
PhSeH	142.2

Table 2. Relevant ^{119}Sn-NMR Chemical Shifts

compound	δ (C_6D_6)
Bu_3SnH	−88.4
$Bu_3SnSePh$	60.2
Bu_3SnPh	−42.7
$Bu_3SnSnBu_3$	−83.4
Bu_3SnBr	134

A distinct advantage of this method lies in the introduction of PhSeH in the form of PhSeSePh. This eliminates the need to prepare and handle PhSeH which is extremely air sensitive and a vesicant.[9] Aside from avoiding the use of a very unpleasant substance, this removes any doubt as to the contamination of PhSeH by PhSeSePh and to the actual concentration of PhSeH used, an uncertainty which caused Newcomb and coworkers to analyze all samples of PhSeH by GLC immediately before use.[10] A similar concept for radical kinetics has previously been put forward by Newcomb,[2c] based on Roberts original work,[6] in which a catalytic quantity of thiol, as hydrogen atom donor, is recycled by reaction with a silane. Competing addition of the thiol and silane to alkenes, however, caused Newcomb to abandon this approach.

Scheme 1 would be complicated if $PhSeSnBu_3$ were to react with Bu_3SnH (eq 5) as this would double the concentration of PhSeH in the reaction mixture and lead to an error of a factor of two in any rate constants determined.

$$PhSeSnBu_3 + Bu_3SnH \rightarrow PhSeH + Bu_3SnSnBu_3 \quad (5)$$

This is clearly not the case. Alkyl phenyl selenides[1] and acyl phenyl selenides[11] are excellent precursors to alkyl and acyl radicals, respectively, for radical cyclizations, when used in conjunction with Bu_3SnH. If eq 5 were to operate, not only would 2 mol equiv of stannane be required to consume the substrate in these reactions, but also the stoichiometric quantites of PhSeH generated would be more than sufficient to prevent any rearrangements from occurring.[5] Firm evidence was provided by a combination of ^{77}Se-NMR[12] and ^{119}Sn-NMR[13] experiments with relevant chemical shifts grouped in Tables 1 and 2. A 0.4 M solution of PhSeSePh in C_6D_6 was treated at room temperature under Ar with 1 mol equiv of Bu_3SnH resulting in immediate decolorization. In the ^{77}Se-NMR spectrum two new signals in a 1:1 ratio at δ 142.2 and −27.7 ppm were formed and attributed with the aid

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[6] (a) Allen, R. P.; Roberts, B. P.; Willis, C.; R. *J. Chem. Soc., Chem. Commun.* **1989**, 1387. (b) Cole, S. J.; Kirwan, J. N.; Roberts, B. P.; Willis, C. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 103. (c) Dang, H.-S.; Roberts, B. P. *Tetrahedron Lett.* **1995**, *36*, 2875.

[7] For early examples of this principle involving decarbonylation of aldehydes catalyzed by thiols see: (a) Harris, E. F. P.; Waters, W. A. *Nature* **1952**, *170*, 212. (b) Harris, E. F. P.; Waters, W. A. *Discussions Farad. Soc.* **1953**, *14*, 221. (c) Berman, J. D.; Stanley, J. H.; Sherman, W. V.; Cohen, S. G. *J. Am. Chem. Soc.* **1963**, *85*, 4010.

[8] An alternative explanation for this type of catalysis has recently been advanced: Zavitsas, A. A.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1995**, *117*, 10645.

[9] Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: Oxford, 1986; p 26.

[10] Newcomb, M.; Manek, M. B.; Glenn, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 949.

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[12] McFarlane, H. C. E.; McFarlane, W In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic: New York, 1983; Vol. 2, p 275.

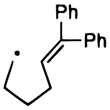
[13] (a) Harris, R. K.; Kennedy, J. D.; McFarlane, W. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic: London, 1978; p 342. (b) Smith, P. J.; Tupciauskas, A. P. *Annu. Rep. NMR Spectrosc.* **1978**, *8*, 291.

of authentic samples to PhSeH and $PhSeSnBu_3$, respectively, whereas the ^{119}Sn-NMR spectrum showed a single signal at δ 60.2 due to $PhSeSnBu_3$.[14] It is clear that equimolar quantities of Bu_3SnH and PhSeSePh react very rapidly in a stoichiometric manner according to eq 1. In a second experiment, an authentic sample[15] of $PhSeSnBu_3$ was treated with 1 mol equiv of Bu_3SnH and heated to 80 °C in C_6D_6 for 1 h. Examination of the reaction mixture by ^{77}Se- and ^{119}Sn-NMR revealed that no reaction had taken place. It is therefore clear that there is no further reaction at 80 °C between $PhSeSnBu_3$ and additional Bu_3SnH, i.e. eq 5 is not valid.

In order to test the proposed kinetic scheme we elected to redetermine the rate constant of an established radical clock. The rearrangement of the 6,6-diphenyl-5-hexenyl radical **1** to the cyclopentyl diphenylmethyl radical **2** was selected for this purpose. The rate constant for this rearrangement has been determined[16] by Newcomb using his PTOC adaptation[2c] of the Barton *O*-acyl thiohydroxamate chemistry,[17] indirectly by trapping with thiols. The calculated rate constant at 20 °C, as determined from the Arrhenius function, is 5×10^{7} s^{-1}. More recently, Newcomb has reported an updated Arrhenius function (eq 6) for this cyclization using the LFP method leading to a rate constant of 4×10^7 s^{-1} at 20 °C.[18]

$$\log(k_R) = 9.8 - 3.0/2.3RT \qquad (6)$$

Appropriate concentrations of **3** and PhSeSePh for the obtention of readily measureable ratios of the **4**:**5** on treatment with Bu_3SnH were established through preliminary experiments. A stock solution of PhSeSePh in benzene was used to prepare seven flasks containing a set amount of **3** and between 5 and 35 mol % of PhSeSePh, which were then made up to 100 mL. A quantity of Bu_3SnH equal to that of PhSeSePh was then added to each flask such that the yellow solution was decolorized and PhSeH was generated quantitatively (eq 1). After purging with Ar the flasks were placed, one by one, in a water bath at 20 °C in a Rayonet photoreactor and irradiated for 1.5 h during which time Bu_3SnH (110 mol % with respect to **3**) and AIBN were added dropwise with the aid of a motor-driven syringe pump. The solvent was then removed under vacuum and the ratio of **4**:**5** determined by integration of the olefinic signal of **4** against the benzhydryl signal of **5** in the ^{1}H-NMR spectrum. In each experiment **3** was completely consumed. Depletion of the catalyst by addition to the double bond present in **3** and **4** was not observed, presumably owing to the reverse reaction being more rapid than quenching of the adduct radical under the dilute conditions used. The data are collected in Table 3. A plot of **4**/**5** against molar concentration of PhSeSePh is a straight line of slope 29 ± 3.2,[19] passing tolerably close to the origin with an intercept of −0.058 ± 0.05. The slope of the plot is equal to k_H/k_R where k_H is the rate constant for the reaction of **1** with PhSeH and k_R that of cyclization. Substituting 1.98×10^9 for k_H at 20 °C[20] gives $k_R = 6.8 \times 10^7$ s^{-1} at 20 °C. This rate constant is in fair agreement with that obtained by Newcomb and serves to validate the proposed method. Nevertheless, it is appropriate to ask why better agreement with the literature values for this cyclization is not found? One possible source of error lies in the position of the equilibrium described by eq 4, which will depend to some extent on the relative bond dissociation energies (BDE's) of Sn−H and Se−H. The BDE of Me_3Sn-H is 74 kcal mol^{-1};[21] estimates for that of PhSe−H vary between 67[22] and 74[23] kcal mol^{-1}. In order to probe this possibility parallel cyclizations of **3** were carried out, under the standard conditions, using on the one hand Bu_3SnH and, on the other, Ph_3SnH with its higher rate of trapping of primary alkyl radicals ($k_{25} = 5 \times 10^6$ M^{-1} s^{-1})[24] and therefore weaker Sn−H bond. Within the limits of experimental error, both runs gave the same ratio of **4**:**5** suggesting that the equilibrium (eq 4) lies fully to the right and hence that the effective concentration of PhSeH is the same as that of the PhSeSePh administered initially. This is readily understood in terms of the equilibrium (eq 4) being constantly driven to the right by the removal of $Bu_3Sn\bullet$ following its reaction with the radical precursor RX, in this case **3**. Several experiments using a set concentration of PhSeSePh and in which the reaction was stopped at different stages of conversion were also conducted. Within the limits of experimental error, the ratio **4**:**5** was found not to vary with conversion, indicating that the concentration of PhSeH is constant throughout the course of the reaction. A further plausible source of error lies in k_H, the rate constant for trapping of a primary alkyl radical by PhSeH,[4] determined by the PTOC/PhSeH method with all the disadvantages of using stoichiometric PhSeH outlined above. Evidently, it is possible to take the, obviously accurate, LFP rate constant $k_R = 4 \times 10^7$ s^{-1} for the cyclization of **1** and the slope from the above plot and calculate a new value for



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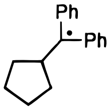

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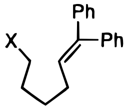

3: X = Br
4: X = H

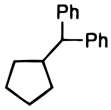

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Table 3. Reaction of 3 with Bu_3SnH and PhSeSePh at 20 °C

mol % PhSeSePh	[PhSeH] (M × 10^3)	ratio **4**/**5**
5	3.1	0.029
10	6.2	0.14
15	9.6	0.21
20	12.4	0.30
25	15.5	0.39
30	18.6	0.51
35	21.7	0.56

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[14] Addition of a further 1 equiv of Bu_3SnH results in a second slow reaction, incomplete after several days at room temperature, which results in the gradual consumption of PhSeH and Bu_3SnH with slow evolution of a colorless gas and formation of a grey precipitate, presumed to be Se metal.

[15] (a) Fukuzawa, S.; Niimoto, Y.; Fujinami, T.; Sakai, S. *Heteroat. Chem.* **1990**, *1*, 491. (b) Macmullin, E. C.; Peach, M. E. *J. Organomet. Chem.* **1973**, *52*, 355.

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[17] Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901.

[18] Newcomb, M.; Horner, J. H.; Filipowski, M. A.; Ha, C.; Park, S.-U. *J. Am. Chem. Soc.* **1995**, *117*, 3674.

[19] Errors are given at the 95% confidence interval (3.2σ for the results obtained here with a small data set and 2σ for those of Newcomb with a much larger data set).

[20] Calculated from the combined (THF + toluene) Arrhenius parameters [$\log(k_H) = 10.87 - 2.10/2.3RT$] for trapping of a primary alkyl radical by PhSeH.[4]

[21] Griller, D.; Kanabus-Kaminska, J. M.; Maccoll, A. *J. Mol. Struct. (THEOCHEM)* **1988**, *163*, 125.

[22] See footnote 34 in ref 10.

[23] Newcomb, M. Private communication. This value is based on a BDE for PhS−H of 85 kcal.mol^{-1} rather than that of 78 used in ref 10.

[24] Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *94*, 6059.

Table 4. Determination of Arrhenius Function for $RCH_2\bullet$ with PhSeH in Toluene

temp (°C)	[PhSeH] (M × 10^3)	ratio **4**/**5**	k_H/k_R	k_H (× 10^{-8} s^{-1})
20	–	–	33.3[a]	12.0[a]
0	4.6	0.14	30.4	7.6
−20	4.6	0.20	43.5	7.0
−42	4.6	0.25	54.3	5.0
−62	4.6	0.32	69.6	3.4

[a] Calculated using the data from Table 3 (in benzene).

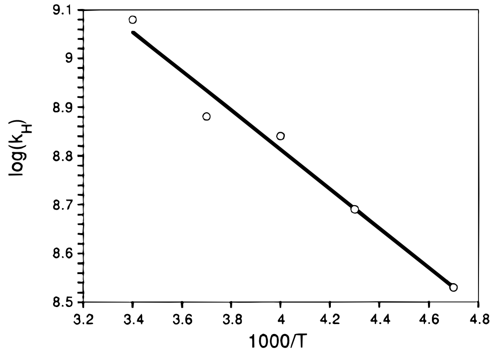


Figure 1. log (k_H) vs 1000/T.

the trapping of primary alkyl radicals by PhSeH at 20 °C in benzene. Such a calculation gives $k_H = 1.2 \times 10^9$ M^{-1} s^{-1} at 20 °C. Equally, it was possible to conduct the cyclization of **3** using our catalytic PhSeSePh/Bu_3SnH method over an 80 °C range of temperature (Table 4) and so determine a relative Arrhenius function (eq 7) for the cyclization and trapping of **1** with PhSeH in toluene. Addition of eq 6 then leads to the Arrhenius function (eq 8, Figure 1) for trapping of the primary alkyl radical **1** by PhSeH in toluene. Comparison of this function with that obtained by Newcomb by the PTOC/PhSeH method in toluene as solvent (eq 9) shows that, at the 95% confidence interval, the two methods are in excellent agreement.[25]

$$\log(k_H/k_R) = 0.55\ (\pm 0.56) + 1.24\ (\pm 0.64)/2.3RT \quad (7)$$

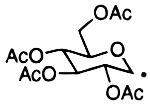
$$\log(k_H) = 10.35\ (\pm 0.58) - 1.76\ (\pm 0.64)/2.3RT \quad (8)$$

$$\log(k_H) = 10.88\ (\pm 0.19) - 2.06\ (\pm 0.24)/2.3RT \quad (9)$$

With the validity of the method established we applied it to the determination of the rate constant for hydrogen atom abstraction from PhSeH by a substituted alkyl radical. The β-(acetoxy)alkyl migration of the tetra-*O*-acetylglucopyranos-1-yl radical **6** to **7** was chosen for this purpose. The rate constant for this migration in benzene at 75 °C has been determined to be 4.0×10^{2} s^{-1} by Sustmann, Giese, and co-workers using the kinetic ESR method.[26] The experiment was conducted essentially as in the above example, except that it was run in benzene at reflux, and that the slower clock reaction required the use of lower amounts of PhSePh. This experiment was conducted in duplicate. In both runs all the substrate **8**[27] was consumed. The data is presented in Table 5. Plots of **9**:**10** against molar concentration of PhSeSePh gave straight lines of gradient 8.5 ± 1.0 × 10^3 and 9.5 ± 0.3 × 10^3 for the two runs, respectively.[19] The weighted mean gradient[28,29] for the two runs is 8.9 ± 1.2 × 10^3 from which the rate constant for hydrogen atom abstraction from PhSeH by radical **6** is calculated to be 3.6 ± 0.5 × 10^6 M^{-1} s^{-1}. The relatively large difference in slope between the two runs is probably best attributed to inaccuracies in the preparation of the two stock solutions. In this respect we note that the rearrangement of **6** to **7** is rather slow compared to other preparatively useful radical processes, making the ratio of **9**:**10** and the slope of the above plots very susceptible to changes in the concentration of PhSeH used. As such the method described here can be expected to be less accurate for determination of the kinetics of slower processes.

Table 5. Reaction of 8 with Bu_3SnH and PhSeSePh

mol % PhSeSePh	[PhSeH] (M × 10^4)	ratio **9**/**10** (run 1)	ratio **9**/**10** (run 2)
3	2.9	3.1	3.4
4	3.9	4.2	4.3
5	4.9	4.9	5.3
6	5.9	5.7	6.2
7	6.8	6.5	7.1



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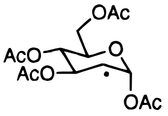

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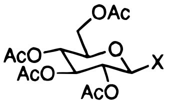
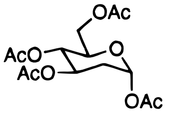
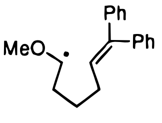


8: X = SePh
9: X = H



10

This rate constant is substantially smaller than that for the reaction of a primary alkyl radical with PhSeH (vide supra). Hence, it is of some interest to note the recent work of Newcomb on the rate constants for the trapping of radical **11** by t-BuSH as well as for its cyclization. Both hydrogen atom abstraction from t-BuSH and cyclization were found to have essentially the same rate constants as the equivalent reactions of **1**.[30] This was attributed to the favorable polar characteristics for the two reactions overriding any stability provided to **11** by resonance with the methoxy group. The slower rate of hydrogen atom abstraction from PhSeH by **6** cannot therefore simply be attributed to stabilization by the ring oxygen. Radical **6** is known to exist in a boatlike conformation (Figure 2) in which the single electron is



11

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[25] As noted by Newcomb the activation parameters in eqs 8 and 9 are such that trapping by PhSeH must be partially diffusion controlled in low viscosity solvents. For a full discussion of this point see ref 4a.

[26] Korth, H.-G.; Sustmann, R.; Groninger, K. S.; Leisung, M.; Giese, B. *J. Org. Chem.* **1988**, *53*, 4364.

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[28] Smith, E. D.; Mathews, D. M. *J. Chem. Ed.* **1967**, *44*, 757.

[29] Errors given for the 95% confidence interval (2.3σ).

[30] Johnson, C. C.; Horner, J. H.; Tronche, C.; Newcomb, M. *J. Am. Chem. Soc.* **1995**, *117*, 1684.

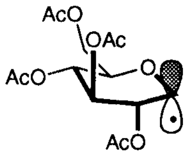


Figure 2.

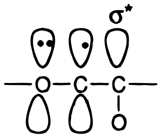
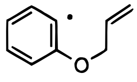


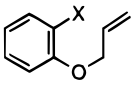
Figure 3.

periplanar with one lone pair from the ring oxygen and with the antibonding σ^* orbital of the adjacent C−OAc bond resulting in what is assumed to be a stabilizing extended anomeric effect (Figure 3).[31,32] Presumably, it is this additional stabilization over and above that in **11** which retards the reaction of **6** with PhSeH. Alternatively, it could be argued that the electron-withdrawing β-acyloxy group renders the anomeric radical less nucleophilic and in doing so removes the advantage of a polarity matched reaction with PhSeH.

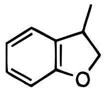
Finally, we note that attempts at the trapping of the aryl radical **12**, generated from the iodide **13**,[33] using the Bu_3SnH/PhSeSePh couple were fruitless. Experiments using as much as 30 mol % of PhSeSePh gave less than 5% of **14** as compared to the cyclization product **15**. The estimated[34] rate constant for cyclization of **12** is 5.3×10^9 s^{-1} and although this is two orders of magnitude greater than that for the cyclization of **1** to **2** it is well within the range initially intended by Newcomb in his original studies of trapping by PhSeH.[4] This failure is therefore probably best attributed to the unfavorable polar characteristics of the hydrogen atom abstraction reaction between an electrophilic aryl radical and the acidic PhSeH.



12



13: X = I
14: X = H



15

Experimental Section

General. ^{1}H-NMR spectra were recorded at 300 MHz and ^{13}C-NMR spectra at 75 MHz with chemical shifts (δ) downfield from tetramethylsilane as internal standard; J-values are given in Hz. ^{77}Se-NMR and ^{119}Sn-NMR spectra were recorded at 38.2 and 74.6 MHz, respectively, with chemical shifts referenced to Me_2Se and Me_4Sn, respectively. Microanalyses were performed by Midwest Microanalytical, Indianapolis, IN. All solvents were dried and distilled by standard techniques. Tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone ketyl before use.

Reaction of Bu_3SnH and PhSeSePh. PhSeSePh (62 mg, 0.2 mmol) was dissolved in C_6D_6 (0.5 mL) under Ar in a 5 mm NMR tube and the ^{77}Se-NMR spectrum recorded. Bu_3SnH (54 μL, 0.2 mmol) was added by syringe, resulting in immediate decolorization of the yellow solution. The ^{77}Se- and ^{119}Sn-NMR spectra were recorded. Addition of further Bu_3SnH (54 μL, 0.2 mmol) caused a gradual evolution of a colorless gas and the appearance of a metallic grey prepicipitate. This reaction, which resulted in slow consumption of PhSeH and of Bu_3SnH as judged by ^{77}Se- and ^{119}Sn-NMR spectroscopy, respectively, was incomplete after several days at room temperature.

Attempted Reaction of $PhSeSnBu_3$ and Bu_3SnH. An authentic sample of $PhSeSnBu_3$ (89 mg, 0.20 mmol) was dissolved in C_6D_6 (0.5 mL) under Ar in a 5 mm NMR tube and the ^{77}Se-NMR spectrum recorded. Bu_3SnH (54 μL, 0.20 mmol) was then added and the tube heated to 80 °C for 1 h. After cooling the ^{77}Se- and ^{119}Sn-NMR spectra were recorded.

6-Bromo-1,1-diphenyl-1-hexene (3). To a solution of (5-hydroxypentyl)triphenylphosphonium bromide[35] (2.54 g, 5.9 mmol) in THF (40 mL) was added n-butyllithium (6.5 mL, 2M in pentane) with stirring at −78 °C under Ar. The reaction mixture was allowed to warm to room temperature, stirred for a further 20 min, and then treated dropwise with a stirred solution of benzophenone (1.20 g, 6.58 mmol) in THF (15 mL). After stirring for 10 h at room temperature, water (5 mL) was added and the solvent removed under vacuum. The residue was taken up in water (15 mL) and dichloromethane (40 mL), the organic layer separated, and the aqueous layer extracted with dichloromethane (2 × 40 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated to give a residue, which after chromatography on silica gel (eluent: hexane/ethyl acetate 20/1) gave 1,1-diphenyl-1-hexen-6-ol as a colorless oil (1.39 g, 93%). ^{1}H-NMR, δ: 7.28 (10H, m), 6.08 (1H, t, J = 7.46), 3.59 (2H, t, J = 5.57), 2.16 (2H, m), 1.55 (4H, m), 1.25 (1H, bs); ^{13}C-NMR, δ: 142.7, 141.8, 140.1, 129.6, 128.1, 128.0, 127.2, 126.7, 126.6, 62.6, 32.2, 29.4, 26.0. This alcohol (1.80 g, 7.15 mmol) and pyridine (0.57 g, 7.25 mmol) were dissolved in dichloromethane (10 mL) and added to a suspension of triphenylphosphine dibromide in dichloromethane formed by dropwise addition of bromine in tetrachloromethane (2 M, 3.6 mL, 7.25 mmol) to a stirred solution of triphenylphosphine (1.90 g, 7.25 mmol) under Ar in dichloromethane (15 mL). After stirring for 1 h at room temperature the precipitate was filtered off and the filtrate poured into water (10 mL). The organic layer was run off and the aqueous layer further extracted with dichloromethane (2 × 20 mL). The extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give a residue, which after chromatography on silica gel (eluent: hexane/ethyl acetate 20/1) yielded **3** as a colorless oil (1.70 g, 76%). ^{1}H-NMR, δ: 7.27 (10H, m), 6.06 (1H, t, J = 7.46), 3.34 (2H, t, J = 6.76), 2.14 (2H, dt, J = 7.43, 7.40), 1.85 (2H, m), 1.59 (2H, m); ^{13}C-NMR, δ: 142.5, 142.2, 140.0, 129.8, 129.0, 128.2, 128.1, 127.1, 126.9, 126.9, 33.6, 32.2, 28.7, 28.3; IR υ_{max}: 3059, 2958, 1598 cm^{-1}. Anal. Calcd for $C_{18}H_{19}Br$: C, 68.58; C, 6.07. Found: C, 68.61; H, 6.07.

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[31] (a) Beckwith, A. L. J.; Brumby, S. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1801. (b) Dobbs, A. J.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 786. (c) Gilbert, B. C.; Trenwith, M.; Dobbs, A. J. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1772.

[32] (a) Dupuis, J.; Giese, B.; Rüegge, D.; Fischer, H.; Korth, H.-G.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 896. (b) Korth, H. G.; Sustmann, R.; Dupuis, J.; Giese, B. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1453.

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Kinetics of Rearrangement of 3. A stock solution of **3** (4.00 g) in benzene (40 mL) was prepared and 2 mL (0.634 mmol) transferred to each of seven 25 mL pear-shaped Pyrex flasks. A stock solution of PhSeSePh (0.28 g) made up to 28 mL in benzene was then used to add 5, 10, 15, 20, 25, 30, or 35 mol % of PhSeSePh to these flasks. An amount of Bu_3SnH corresponding to that of PhSeSePh was added to each flask and the volume made up to 10 mL. A steady stream of Ar was then passed through each flask for several minutes. Each flask was then immersed, sequentially, in a circulating water bath maintained at 20 °C in a Rayonet photoreactor (254 nm) and irradiated, with stirring under Ar, while 0.5 mL of a stock solution of Bu_3SnH (2.22 g, 7.6 mmol) and AIBN (0.10 g, 0.63 mmol) made up to 5 mL in benzene was added dropwise with a motor-driven syringe pump over 50 min. Irradiation was continued at 20 °C for a further 0.5 h before the solvent was removed *in vacuo* and the residue examined by ^{1}H-NMR. In each case the substrate was completely consumed. Integration of the olefinic signal (**4**, C═C*H*) at δ 6.09 and of the benzhydryl signal (**5**, Ph_2CH) at δ 3.57 gave the ratio of **4**/**5** as recorded in Table 3. The spectral data for **4** and **5** were identical to those recorded in the literature.[16] The total volume change in the course of the reaction, owing to the addition of Bu_3SnH, was essentially negligible at 5%. In calculating the molar concentration of PhSeSePh and so of PhSeH a mean volume of 10.25 mL was taken.

Determination of the Arrhenius Parameters for Quenching of Radical 1 with PhSeH. A stock solution of **3** (1.60 g) in toluene (16 mL) was prepared and 1 mL (0.32 mmol) transferred to each of four 25 mL round-bottomed flasks. A stock solution of PhSeSePh (0.35 g) in toluene (35 mL) was made up and 1.5 mL (0.048 mmol) added to each flask, followed by Bu_3SnH (1.67 mL of a 0.03 M solution in toluene, 0.057 mmol). Each flask was then made up to 10 mL with toluene and purged with a steady stream of Ar for several minutes. In turn, each flask was equilibrated at the required temperature (Table 4) and irradiated with 100 W medium pressure Hg lamp (through Pyrex) while Bu_3SnH and AIBN in toluene (0.5 mL of a stock solution containing 2.22 g, 7.6 mmol of Bu_3SnH and 0.19 g, 0.63 mmol of AIBN in a total of 10 mL) was added with the syringe pump over 50 min. After the addition the irradiation was continued for a further 0.5 h before the solvent was removed under vacuum and the residue examined by ^{1}H-NMR to give the data recorded in Table 4. The data for 20 °C were taken from Table 3. In calculating the molar concentration of PhSeSePh and so of PhSeH a mean volume of 10.25 mL was taken.

Kinetics of Rearrangement of 8. Five flasks were made up, using stock solutions, containing **8** (97.5 mg, 0.2 mmol), PhSeSePh (3, 4, 5, 6, or 7 mol %) and Bu_3SnH (3, 4, 5, 6, or 7 mol %) in benzene (20 mL) essentially as decribed above for the rearrangement of **3**. After purging with Ar, each flask was brought to reflux under Ar and treated dropwise (syringe pump) with Bu_3SnH (0.070 g) and AIBN (1.6 mg) in benzene (1 mL) over 2.33 h. Reflux was maintained for a further 1 h before the solvent was removed under vacuum and the residue examined by ^{1}H-NMR. In each case the substrate was completely consumed. Integration of the resonances at δ 3.31 (**9**, H-1axial) and 6.26 (**10**, H-1) gave the ratios of **9**/**10** in Table 5. The spectral data of **9** and **10** were identical with those in the literature.[36] In calculating the molar concentration of PhSeSePh and so of PhSeH a mean volume of 20.5 mL was taken.

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Supporting Information Available: Plots of **4**:**5** versus [PhSeH] and of **9**:**10** versus [PhSeH] (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[36] Beckwith, A. L. J.; Duggan, P. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1672.