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Picosecond Radical Kinetics. Bond Cleavage of the Cubylcarbinyl Radical

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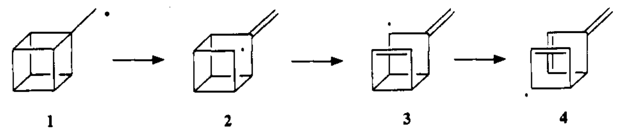
Abstract: Rate constants for the initial bond cleavages of the cubylcarbinyl radical (**1**) were determined by competition kinetics using benzeneselenol as a trapping agent. Measurements over the temperature range −78 to 25 °C gave a temperature-dependent function of $\log (k_r{\cdot}s) = 13.16 - 3.72/2.3RT$. The rate constant for the initial ring opening of radical **1** at 25 °C is 2.9×10^{10} s^{-1}, which ranks this reaction as one of the fastest radical rearrangements known. The putative product of the initial cleavage reaction, the methylenesecocubyl radical **2**, apparently suffers an even faster bond cleavage reaction estimated to be $>1.5 \times 10^{11}$ s^{-1} at 25 °C. The potential utility of methylcubane as a mechanistic probe for oxidation processes that might involve initial hydrogen atom abstraction is noted.

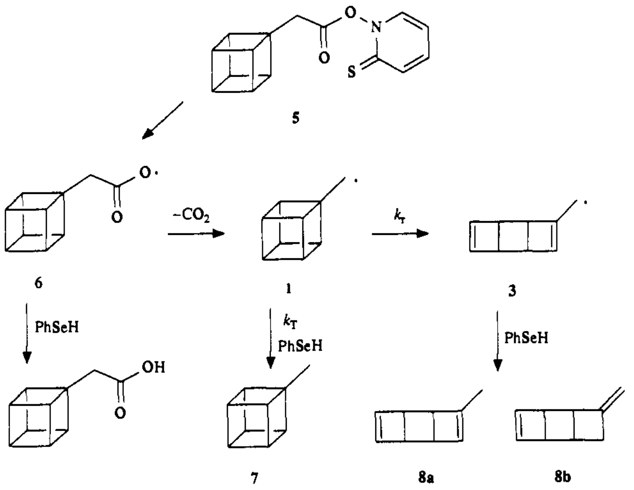
Unimolecular rearrangements of radicals have been widely applied as radical clocks and mechanistic probes. In a radical clock[2] application, a known rate constant for a rearrangement and the distribution of products formed when the rearrangement competes with another (usually bimolecular) reaction can be used to determine the kinetics of the competition reaction; here the desired rate of rearrangement is largely determined by the rate of the competition reaction. In the case of a mechanistic probe application, the production of rearranged products implicates a radical intermediate in a reaction pathway, and one usually desires especially fast radical rearrangements so that competing reactions will not intercept the first-formed radical intermediate before rearrangement. The cyclopropylcarbinyl radical ring opening ($k = 1 \times 10^8$ s^{-1} at 25 °C) is the archetypal fast radical rearrangement and the most accurately calibrated.[3]

Recently, Eaton and Yip reported the production and rearrangement reactions of the cubylcarbinyl radical (**1**).[4] The cubyl system contains a tremendous amount of potential energy with the result that radical **1** reacts in the cascade of bond cleavage processes shown in Scheme I. Initial cleavage of one of three equivalent bonds in radical **1** to give the putative intermediate methylenesecocubyl radical **2** is followed by very rapid (or possibly simultaneous) cleavage of another bond to give intermediate **3**, which could be intercepted by radical-trapping agents. In a slower reaction, intermediate **3** suffers a third bond cleavage to give radical **4**. The initial ring-opening reactions of **1** are very fast; Eaton and Yip determined[4] that conversion of **1** to **3** in benzene at 20 °C occurred with a rate constant of about 2×10^{10} s^{-1}, which would make the initial cleavage reaction one of the fastest known radical reactions involving bond breakage and one that might be quite useful in mechanistic probe studies.[5] In this work, we report detailed kinetic studies of the initial ring-opening reaction of the cubylcarbinyl radical.

Scheme I



Scheme II



Results and Discussion

The method used was the kinetic adaptation of Barton's PTOC ester radical precursors[6] which was reported by Newcomb and Glenn (Scheme II).[3d] PTOC ester **5** reacted in a radical chain reaction to give acyloxy radical **6**, which in turn decarboxylated to give radical **1**. Hydrogen atom transfer from the fast radical trapping agent benzeneselenol[7] was employed as the competing basis bimolecular reaction over a wide temperature range. Hydrogen atom transfer to **1** from PhSeH gave methylcubane (**7**) in competition with the initial cleavage reaction(s) of **1** which produced radical **3**. Trapping of **3** by PhSeH gave tricyclic dienes **8**. The PhSe• radical formed in the trapping reactions reacted with PTOC ester **5** in a radical chain propagation step. As observed previously,[7] PhSeH also trapped a portion of the acyloxy radical **6** in competition with the decarboxylation reaction.

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(1) (a) Wayne State University. (b) The University of Chicago.

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

(3) (a) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024. (b) Mathew, L.; Warkentin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7981. (c) Beckwith, A. L. J.; Bowry, V. W.; Moad, G. *J. Org. Chem.* **1988**, *53*, 1632. (d) Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275. (e) Beckwith, A. L. J.; Bowry, V. W. *J. Org. Chem.* **1989**, *54*, 2681.

(4) Eaton, P. E.; Yip, Y. C. *J. Am. Chem. Soc.* **1991**, *113*, 7692.

(5) That the initial cleavage of **1** is followed by an even faster (or simultaneous) second bond cleavage to give **3** is an unusual and potentially important point in regard to mechanistic studies because the second reaction results in partial localization of spin density in radical **3** on the same carbon atom as in radical **1**. Therefore, if radical **1** was produced in a confined environment that precluded molecular rotation, then the two reactions that convert **1** to **3** would permit a follow-up radical reaction that might not be possible with a mechanistic probe such as cyclopropylcarbinyl in which spin density in the product radical does not reside on the initial radical center. The potential utility of such mechanistic probes for studies of possible radical-forming reactions of enzymes was recently exposed by Branchaud, Glenn, and Stiasny, who coined the term "round-trip radical probe" to describe this class of probes (cf.: Branchaud, B. P.; Glenn, A. G.; Stiasny, H. C. *J. Org. Chem.* **1991**, *56*, 6656).

(6) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901.

(7) (a) Newcomb, M.; Manek, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 9662. (b) Newcomb, M.; Varick, T. R.; Ha, C.; Manek, M. B.; Yue, X. Submitted for publication.

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Table I. Benzeneselenol Trapping Reactions in THF[a]

temp[b] (°C)	$[PhSeH]_m$[c]	% yield[d]	[**7**]/[**8**]	k_T/k_r (M^{-1})[e]	k_r (s^{-1})[f]
25	0.40	67	0.029		
	0.68	62	0.046		
	0.70	61	0.053		
	1.15	59	0.097		
	1.62	63	0.130		
	2.24	68	0.173	0.080 (6)	2.9×10^{10}
0	0.36	76	0.048		
	0.63	60	0.072		
	0.91	68	0.113		
	1.15	62	0.134		
	2.00	56	0.241		
	2.24	61	0.257	0.115 (6)	1.42×10^{10}
−42	0.19	43	0.037		
	0.42	51	0.082		
	0.71	46	0.118		
	0.99	37	0.213		
	1.41	62	0.274		
	2.15	54	0.434	0.21 (2)	3.6×10^{9}
−78	0.18	64	0.057		
	0.34	41	0.106		
	0.36	58	0.112		
	0.69	48	0.206		
	1.06	42	0.288		
	1.41	50	0.349		
	1.94	60	0.584	0.28 (4)	1.08×10^{9}

[a] Initial concentration of PTOC **5** was 0.017–0.022 M. [b] ±1 °C. [c] Mean concentration of trapping agent. [d] Percent yield of **7** + **8a** + **8b** determined against an internal standard of octane. [e] Ratio of rate constants; the error limits in parentheses are 2 standard deviations for the last significant figure. [f] Rate constant for cubylcarbinyl bond cleavage calculated with k_T from eq 2.

Previous work[4] had shown that PhSeH can trap radical **1** in competition with the initial cleavage reaction. Thus, reaction of PTOC ester **5** in the presence of 1.7 M PhSeH in benzene-d_6 at 20 °C gave **7** in ca. 9% yield and dienes **8** in ca. 60% yield as determined by NMR integration against an internal standard.[4] At this concentration of PhSeH, there was no evidence of products derived from trapping of putative radical **2**. Although radical **3** can further react in the presence of relatively slow trapping agents, Eaton and Yip showed that, even at a concentration as low as 68 mM, PhSeH trapped **3** before further ring opening occurred.[4]

In this work, the yields of products were determined by GC. Methylcubane was identified by GC retention time and GC–mass spectral comparison to an authentic sample.[4,8] On a low-polarity, wide-bore capillary column, methycubane eluted between products **8a** and **8b**, which were identified by their mass spectra and by analogy to the NMR kinetic study of Eaton and Yip and which were previously isolated and characterized by NMR spectroscopy.[4] The relative yields of the components as a function of PhSeH concentrations were consistent with the structure assignments.

Radical chain reactions of PTOC ester **5** in THF in the presence of PhSeH were conducted at temperatures from −78 to 25 °C. For GC analyses, the reaction mixtures contained an internal standard of octane. Table I contains the yields of methylcubane (**7**) and dienes **8** and the ratios of products from these reactions.

As noted above, PhSeH has been shown to trap acyloxy radicals in competition with decarboxylation. However, this trapping reaction cannot account completely for the reduced yields of **7** plus **8** we observed because the total yields were not well correlated with the inverse of the PhSeH concentration. Some of the scatter in total yields undoubtedly resulted from accumulated errors in the weighings and volumetric transfers of the small amounts of PTOC ester and internal standard used in the reactions; we estimate that these errors could be as great as 25%. It is also likely that the PTOC ester, actually an anhydride of a carboxylic acid and a thiohydroxamic acid, was partially consumed in a polar reaction with PhSeH.[10]

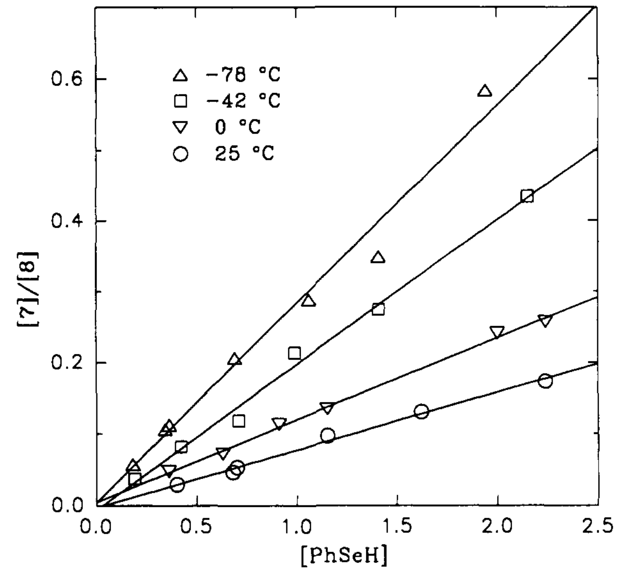

Figure 1. Product ratios from reaction of cubylcarbinyl radical with benzeneselenol.

Irrespective of the origins of the reduced total yields of **7** and **8**, the relative yields of these products are probably considerably more accurate, and all of radical **1** formed in each reaction appeared to be accounted for by the yields of **7** and **8**. This was indicated by plots of the ratio of unrearranged (**7**) to rearranged (**8a** + **8b**) products against PhSeH concentration at each temperature (Figure 1). These plots were linear and had intercepts within 1 standard deviation of 0.

At the relatively high concentrations of PhSeH employed in these studies, the trapping reaction of radical **1** can be treated as a pseudo-first-order process according to eq 1, where k_r is the rate constant for ring opening, k_T is the rate constant for hydrogen atom transfer trapping by PhSeH, and $[PhSeH]_m$ is the average concentration of benzeneselenol during the reaction. In the graphical analyses (Figure 1), the slopes of the plots gave values of k_T/k_r, which are included in Table I.

$$[\mathbf{7}]/[\mathbf{8}] = (k_T/k_r)[PhSeH]_m \qquad (1)$$

In order to calculate the values of the rate constants for ring opening of radical **1**, one must know the values of k_T at each temperature. PhSeH trapping of the cyclopropylcarbinyl radical in solvent THF was found to occur with the Arrhenius function given in eq 2 where the error limits for the last significant figure are 2σ.[7,12] With the assumption that PhSeH trapping of the cubylcarbinyl radical and the cyclopropylcarbinyl radical occur with the same rate constants, one can calculate values for ring opening (k_r) of the cubylcarbinyl radical. These are given in the final column of Table I.[13]

$$\log(k_T{\cdot}M{\cdot}s) = 11.04\ (7) - 2.28\ (9)/2.3RT \qquad (2)$$

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[8] Methylcubane can be prepared readily by the reaction of 1,4-diiodocubane[9a] with methyllithium in the presence of iodomethane.[9b]

(9) (a) Tsanaktsidis, J.; Eaton, P. E. *Tetrahedron Lett.* **1989**, *30*, 6967. (b) Eaton, P. E.; Li, J. Unpublished results.

(10) "Transesterifications" of a PTOC ester by PhSeH and PhSH have been reported.[11]

(11) Gawronska, K.; Gawronski, J.; Walborsky, H. M. *J. Org. Chem.* **1991**, *56*, 2193.

(12) The Arrhenius function in eq 2 for PhSeH trapping in THF differs slightly from that reported originally.[7a] The new function results from further calibration of PhSeH trapping against cyclopropylcarbinyl ring opening and a slight adjustment of the cyclopropylcarbinyl ring opening rate constants.[7b]

(13) It is important to note that PhSeH trapping is about an order of magnitude slower than diffusion and, therefore, will be partially diffusion controlled and a function of the solvent viscosity.[7] Equation 2 provides operational rate constants for cyclopropylcarbinyl trapping in THF and not the actual rate constants for hydrogen transfer. One might be concerned that changes in viscosity due to the large concentrations of PhSeH used in some of the trapping reactions could be important. However, this effect was expected to be manifested as only a small perturbation. The linear functions in Figure 1 show that any viscosity effects were smaller than the scatter in the measurements.

Table II. Results of PhSH Trapping Reactions in THF^a

temp^b (°C)	[PhSH]$_m$^{c}	% **7**^{d}	% **8**^{d}	[**7**]/[**8**]
0	1.18	<0.1	78	
	1.97	<0.1	63	
	2.50	<0.1	56	
−78	1.48	0.7	15.0	0.046
	2.46	1.1	13.3	0.083
	2.48	1.3	14.0	0.093

$^{a-c}$See notes to Table I. ^{d}Percent yields determined against an internal standard.

The assumption that PhSeH trapping of the cubylcarbinyl and cyclopropylcarbinyl radicals occurs with the same rate constant is the weak point of the indirect kinetic study, but there are reasons to believe it is reasonable. For example, the fast radical trapping agent PhSH has been shown to react with a primary radical and cyclopropylcarbinyl radical with the same rate constants,[3d,14] and it is likely that the even more reactive trapping agent PhSeH does so also. Therefore, it is also likely that the reactions of PhSeH with the cubylcarbinyl and cyclopropylcarbinyl radicals will occur with similar rate constants. Further, the small activation energy and large exergonicity for reaction of PhSeH with cyclopropylcarbinyl and other radicals will result in only slight changes in the activation energy for reactions in which the total energy of reaction is similar; one must assume here that the methyl C–H bond energy for methylcubane is similar to the methyl C–H bond energy of methylcyclopropane.

A direct test of the kinetic assumption was possible. We have previously shown that Marcus theory can be used to estimate the rate constants for hydrogen atom transfer trapping of an alkyl radical by the agents *t*-BuSH, PhSH, and PhSeH.[15,16] The analysis does not need to be reproduced here, but the following point is important for this work. If the exergonicity and intrinsic activation energy of the PhSeH trapping of radical **1** were *not* similar to those for PhSeH trapping of the cyclopropylcarbinyl radical, then a significantly different calculated value of k_r would be found when a different trapping agent was employed in trapping **1** with the assumption that the new trapping agent also reacted with cubylcarbinyl and cyclopropylcarbinyl radicals with the same rate constant.

Eaton and Yip reported no trapping of radical **1** by PhSH in a reaction run at room temperature.[4] However, it is well established that bimolecular trapping reactions become more competitive with unimolecular rearrangements as reaction temperatures are reduced (i.e., the activation energies for the trapping reactions are smaller than those of the ring openings). An attempt to trap radical **1** with PhSH at 0 °C did not result in appreciable yields of methylcubane. However, it was possible to trap a small amount of radical **1** with PhSH at −78 °C although the total yields of hydrocarbon product were low due to significant acyloxy radical trapping (Table II). The k_T/k_r values (0.031, 0.034, 0.038 M^{-1}) from eq 1 (with the substitution of [PhSH]$_m$ for [PhSeH]$_m$) were undoubtedly less accurate than the corresponding values from the PhSeH trapping. Nevertheless, when combined with the k_T value for reaction of PhSH with a primary radical at −78 °C (2.9×10^7 M^{-1} s^{-1}),[14] these gave an average value of k_r at −78 °C of 1.0×10^9 s^{-1}, in excellent agreement with the value calculated from the PhSeH trapping results at −78 °C.

The agreement in results with the two trapping agents supports the assumptions (1) that $\Delta G°$ for trapping the cubylcarbinyl radical by each reagent is approximately equal to that for trapping the cyclopropylcarbinyl radical by the same reagent and (2) that the cyclopropylcarbinyl trapping rate constants for PhSeH can be used with confidence in the calculations of cubylcarbinyl bond cleavage reactions. For the bicyclo[2.1.0]pent-2-yl radical, a case where these assumptions were not valid and the exergonicity of the trapping reaction was about 3 kcal/mol greater than that for trapping of cyclopropylcarbinyl, use of the rate constants for PhSH and PhSeH trapping of cyclopropylcarbinyl resulted in values for bicyclo[2.1.0]pent-2-yl ring opening that differed by a factor of 2.[15]

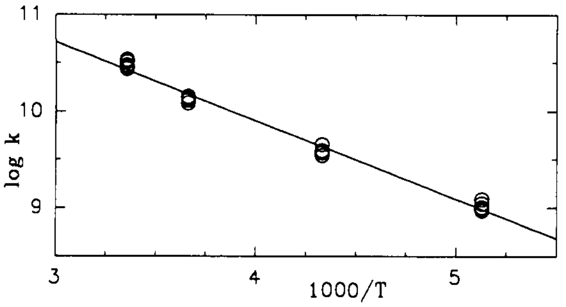

Figure 2. Arrhenius function for bond cleavage of the cubylcarbinyl radical.

The individual k_T/k_r values from Table I and the k_T values for PhSeH trapping in THF (i.e., eq 2) were used to calculate an Arrhenius function for cleavage of cubylcarbinyl radical (Figure 2 and eq 3). In eq 3, the error limits for the last significant figure (2σ) are for the function and do not incorporate estimated errors for PhSeH trapping kinetics.[18]

$$\log (k_r \cdot s) = 13.16\,(14) - 3.72\,(15)/2.3RT \qquad (3)$$

In obtaining the transition state for the initial bond cleavage of the cubylcarbinyl radical, 1 degree of rotational freedom is lost resulting in a decrease in entropy similar to that experienced in the cyclopropylcarbinyl ring opening. On the basis of theoretical grounds[19] and experimental results,[3] the log A term for cyclopropylcarbinyl ring opening is 12.85 per reactive bond;[20] the presence of two equivalent bonds for cleavage increases the actual log A term for cyclopropylcarbinyl to 13.15 (increase by log 2). If we assume that the intrinsic log A for cleavage of radical **1** is also 12.85, then the presence of three equivalent bonds that can suffer initial cleavage leads to a predicted log A term of 13.33. The good agreement between the expected and experimentally determined log A values reinforces our confidence in the kinetic assumptions necessary for calculation of the rate constants for rearrangement.

We had hoped that a study of the ring opening of radical **1** at low temperatures would shed some light on the question of whether putative radical **2** is produced as a discrete intermediate or radical **1** is directly converted to radical **3** by two synchronous bond cleavages. Unfortunately, no evidence of products from trapping of radical **2** was found in this work.[22] It is known that PhSeH reacts with the bicyclo[2.1.0]pent-2-yl radical more rapidly than it reacts with the cyclopropylcarbinyl radical.[15] If we assume that PhSeH would react with radical **2** and the bicyclo[2.1.0]pent-2-yl

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[14] Franz, J. A.; Bushaw, B. A.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 268.

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

[16] Recent ab initio calculations[17] by Fox and Schlegel support this conclusion for hydrogen atom transfers in which charge transfer states are insignificant.

[17] Fox, G. L.; Schlegel, H. B. *J. Phys. Chem.* **1992**, *96*, 298. We thank Professor Schlegel for providing us with a preprint of this paper in advance of publication.

[18] The Arrhenius function in Figure 2 appears to be slightly curved. This is probably an artifact that resulted because the operational Arrhenius function for PhSeH trapping in THF (eq 2) is a linear approximation of a slight curve.[7,13] Because the temperature ranges of the kinetic studies in this work and in the initial measurement of the PhSeH trapping kinetics were about the same, it is not likely that the linear approximation for the PhSeH trapping kinetics introduced a significant error.

[19] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, NY, 1976.

[20] Recently, Bowry, Lusztyk, and Ingold have noted that, for cyclopropylcarbinyl ring opening rate constants, the use of log A = 12.85 per reactive bond and a single accurate rate constant is more likely to provide an accurate Arrhenius function than would be expected from a series of kinetic studies employing a single technique.[21]

[21] Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687.

[22] Previously, Eaton and Yip detected a trace of an unknown compound by NMR studies which might have resulted from trapping of **2**.[4]

radical with similar rate constants (i.e., the exergonicities and intrinsic energies of activation of the two trapping reactions that produce new "cyclobutyl" C–H bonds are similar), then the rearrangement of **2** to **3** must be very fast. Further assuming that the products derived from trapping of **2** would be stable and detectable in 10% yield, the rate constant for this cleavage reaction at 25 °C would exceed 1.5×10^{11} s^{-1}.[23]

In conclusion, we have confirmed the fast cleavage reactions of the cubylcarbinyl radical (**1**) reported by Eaton and Yip[4] and determined more precise rate constants for the initial reaction at several temperatures. At 25 °C, the lifetime of radical **1** is about 35 ps, and the lifetime of putative intermediate **2** at 25 °C appears to be less than 10 ps. Rearrangement of radical **1** will predominate over bimolecular trapping even if the trapping reaction is diffusion controlled and the trapping agent is present in 1 M concentration, and it will be competitive with all but the very fastest first-order processes. The fast ring opening rate constant for radical **1**, the presence in radical **3** of spin density on the original "carbinyl" carbon of radical **1**, and the fact that the methyl C–H bonds in methylcubane are expected to be weaker than the cubyl C–H bonds[24] suggest that methylcubane[9] could be an excellent mechanistic probe for oxidizing reactions that might occur via initial hydrogen atom abstraction from the hydrocarbon.[27]

Experimental Section

Benzeneselenol was prepared by the method of Foster.[28] PhSeH was distilled under subdued light, and the fraction with bp 62–63 °C (7 Torr) was divided into portions and sealed under vacuum in glass vials that were stored at 0 °C in the dark. The purity of each sample of PhSeH was determined by GC before use; typically, the samples were contaminated with Ph_2Se_2 (<5%).

1-[[(Cubylmethyl)carbonyl]oxy]-2(1*H*)-pyridinethione (5) was prepared from cubylacetic acid as previously described.[4] The crude PTOC ester was purified by chromatography on silica gel with ethyl acetate–hexanes elution (1:3, v/v) in a column shielded from light to give **5** in 83% yield: mp 74–75 °C (lit.[4] mp 75 °C dec). The ^1H and ^{13}C NMR spectra matched those reported.[4]

Kinetic Studies. The method used was similar to those previously reported for PhSH and PhSeH trappings with PTOC ester precursors.[3d,8,15] Thus, solutions of PTOC ester **5** and PhSeH or PhSH and octane in THF (freshly distilled from benzophenone–potassium) were prepared in N_2-flushed Pyrex tubes that contained a small stirbar and were shielded from light. The tubes were sealed, and the mixtures 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 ca. 0.5 m from the tubes. After ca. 20 min, the tubes were cooled to −78 °C and opened. The reaction mixtures were analyzed by GC on a 15 m × 0.5 mm DB-5 column (Alltech). The GC injector temperature was maintained at 130 °C; at high injector temperatures, traces of decomposition products (presumed to originate from products **8**) were found to elute in the region of compounds **7** and **8**. The response factor for methylcubane (**7**) relative to octane (0.9) was determined with an authentic sample; the response factors for compounds **8** were assumed to be equal to that of **7**.

Acknowledgment. We thank the National Science Foundation (CHE-8816365, CHE-9117929, and CHE-9010059) for financial support and Professor H. B. Schlegel for helpful discussions.

Registry No. 1, 135191-71-8; **5**, 135191-76-3; phenylselenol, 645-96-5; thiophenol, 108-98-5.

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(23) At 25 °C, PhSeH reacts with the bicyclo[2.1.0]pent-2-yl radical about 5 times faster than it reacts with cyclopropylcarbinyl radical.[15] The hydrogen atom transfer rate constant at 25 °C of about 1×10^{10} M^{-1} s^{-1} will be partially diffusion controlled in THF to give a trapping rate constant of about 7×10^9 M^{-1} s^{-1} or a pseudo-first-order rate constant with 2.2 M PhSeH of about 1.5×10^{10} s^{-1}.

(24) An early calculation (4-31G basis set) of the cubyl C–H bond energy led to an absolute value of 91 kcal/mol.[25a] However, calculations of the isodesmic reactions of eq i indicate that the reactions are endothermic by 11.0 kcal/mol ($R^\bullet = (CH_3)_3C^\bullet$, 6-31G* basis set)[25b] and by 8.4 kcal/mol ($R^\bullet = CH_3CH_2CH_2^\bullet$, 4-31G basis set).[25c] From standard bond dissociation values[26] and the results of the isodesmic calculations, the BDE for cubyl C–H is 104–106 kcal/mol, nearly as great as that of cyclopropane (106 kcal/mol).[26]

$$R^\bullet + \text{cubyl-H} \rightarrow \text{R-H} + \text{cubyl}^\bullet \qquad \text{(i)}$$

(25) (a) Schubert, W.; Yoshimine, M.; Pacansky, J. *J. Phys. Chem.* **1981**, *85*, 1340. (b) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 3227. (c) Schlegel, H. B. Unpublished results.

(26) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(27) Studies aimed at determining the efficacy of methylcubane as a mechanistic probe for investigation of the reaction pathways of P-450-containing enzymes and methane monooxygenase enzymes are in progress. We note that cubylmethanol is a stable compound,[4] but the stabilities of alcohols derived from radical **3** could be problematic.

(28) Foster, D. G. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 772.