while the solution was agitated ultrasonically, affording **10** as a white precipitate in quantitative yield. After removal of the solvent via a syringe, the precipitate was washed with dry hexane (2 × 4 mL), dried under high vacuum, and stored under N_2. According to the ^1H and ^{13}C NMR spectra, **10** prepared in this way is NMR pure. Without ultrasonic agitation, **10** separates from the reaction mixture as a viscous syrup, which can be solidified to a waxy mass only with great difficulty. According to the ^1H and ^{13}C NMR spectra, the waxy solid consisted of >98% pure **10**. See Tables I–III for spectroscopic data of **10**.

Compound 11. Compound **11** was prepared in quantitative yield from 331.6 mg (1.547 mmol) of **7** and 310 μL (1.60 mmol) of $CF_3SO_3SiMe_3$ in 4.4 mL of hexane/benzene (10:1, v/v), according to the procedure outlined for **10**. The only difference in the procedure was that the precipitate of crude **11** was removed by filtration. The purity of the product isolated in this way was 90–95%; mp 50 °C dec. Anal. Calcd for $C_{13}H_{31}N_4F_3O_3Si_2S$ (found): C, 35.76 (34.43); H, 7.16 (7.00); N, 12.83 (13.51). Attempts to purify **11** by recrystallization from $CHCl_3$, C_6H_6, CH_3CN, hexane, or their mixtures yielded only a viscous, polymeric oil when the warm solutions of **11** were cooled in these solvents. Solutions of pure **11** in $CDCl_3$ suitable for NMR spectroscopy were, however, conveniently prepared by reacting stoichiometric quantities of **7** and $CF_3SO_3SiMe_3$ in an NMR tube. The high sensitivity of **11** to nucleophiles is illustrated by the observation that solutions of **11** in $CDCl_3/CD_3CN$ (1:1) decompose at a rate of ca. 5%/h. The NMR data on pure **11** are given in Tables II and III.

Compound 12. A solution of pure **12** in $CDCl_3$ was prepared by adding 113 μL (0.998 mmol) of CF_3SO_3Me to a solution of 380 mg (0.977 mmol) of **9** in 2.3 mL of dry $CDCl_3$ in a 10-mm NMR tube. The reaction mixture was heated to 55 °C for 15 min to ensure completion of the reaction. No attempts were made to isolate **12**. Its NMR data are given in Tables II and III. An attempt to react **9** with $CF_3SO_3SiMe_3$ in $CDCl_3$ failed. When a solution of 27 mg (0.070 mmol) and 27 μL (0.14 mmol) of $CF_3SO_3SiMe_3$ was heated for 10 days at 55 °C, only the reactants plus a small amount (<5%) of polymeric reaction product could be detected by ^1H NMR spectroscopy in the reaction mixture.

Compound 13. Repeated attempts to prepare **13** from **8** and CF_3SO_3Me, according to the procedure described for **10** and **11**, resulted in the isolation of an intractable, moisture-sensitive, waxy semisolid, which according to ^1H and ^{13}C NMR was pure. Attempts to recrystallize the semisolid from a variety of solvent mixtures failed. Solutions of pure **13** in $CDCl_3$ for NMR spectroscopy were prepared as described for **11** and **12**. For NMR data on **13**, see Tables II and III. Cation **13** was generated independently by the reaction of equimolar quantities of **8** and a suspension of $Me_3O^+BF_4^-$ in $CDCl_3$. About 70% conversion to **13** was achieved after 3 days at room temperature. The cations in the $CF_3SO_3^-$ and BF_4^- salts of **13** in the reaction products of **8** with CF_3SO_3Me and with $Me_3O^+BF_4^-$ gave identical ^1H and ^{13}C NMR spectra.

Compounds 14 and 16. A 1:1 mixture of **14** and **16** was precipitated by the slow addition of 287 μL (1.485 mmol) of $CF_3SO_3SiMe_3$ to a solution of 332.5 mg (1.456 mmol) of **8** in 5 mL of hexane. The reaction mixture was then heated to the boiling point, which caused virtually complete dissolution of the precipitate, leaving a small amount of a gumlike residue. The solution was then quickly cooled to room temperature, causing the precipitation of fine, needle-shaped, colorless crystals. Following the removal of the solvent by syringe, the crystals were dried under vacuum, transferred into a drybox, and removed carefully from the gumlike residue. According to the ^1H NMR spectrum, taken immediately after dissolution of the crystalline material in $CDCl_3$, the composition of the product was a 7:3 mixture of **16** and **14**, mp 70–73 °C dec. Anal. Calcd for $C_{14}H_{33}N_4F_3O_3SiS$ (found): C, 37.31 (37.17); H, 7.38 (7.55); N, 12.43 (12.59); Si, 12.46 (12.33). For NMR data, see Tables II and III.

Compound 15. To a solution of 665.5 mg (1.652 mmol) of **2a** in 2.3 mL of $CDCl_3$ were added eight 40-μL portions of CF_3SO_3Me (1.656 mmol). The reaction was monitored by NMR spectroscopy and was found to be complete in 12–16 h. Following the acquisition of the ^1H, ^{13}C, ^{29}Si, and ^{15}N NMR spectra, the solvent was evaporated, leaving a sticky, light brown solid. The solid was washed with diethyl ether (2 × 5 mL) to remove the brown, polymeric side products. Then 8 mL of diethyl ether and the amount (ca. 1 mL) of $CHCl_3$ necessary to effect complete dissolution of the solid were added. The resulting solution was filtered and cooled slowly to ca. −20 °C, affording colorless, feathery crystals of **15**. The yield of pure, crystalline **15** was 50–70%; mp 138–140 °C. Anal. Calcd (found) for $C_{20}H_{51}N_4F_3O_3Si_5S$: C, 38.43 (37.94); H, 8.22 (8.45); N, 8.96 (8.97); F, 9.12 (13.80); Si, 17.70 (22.46); Si + F, 31.59 (31.46).

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Supplementary Material Available: ^{13}C NMR data (1 page). Ordering information is given on any current masthead page.

Ring Opening and Hydrogen Atom Transfer Trapping of the Bicyclo[2.1.0]pent-2-yl Radical

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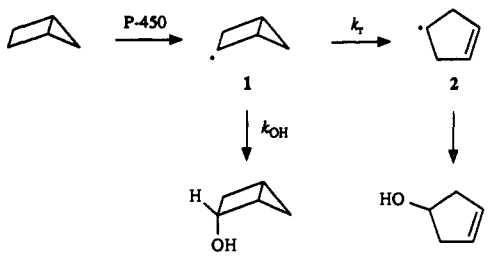
Abstract: Relative rate constants (k_r/k_H) for ring opening of the bicyclo[2.1.0]pent-2-yl radical (**1**) to the cyclopent-3-enyl radical and trapping of radical **1** with *t*-BuSH, PhSH, and PhSeH in solvent THF were measured at temperatures between −78 and 50 °C. The hydrogen atom donors reacted more rapidly with radical **1** than with the cyclopropylcarbinyl radical (**6**). Rate constants for ring opening of **1** (k_r) could be obtained by estimating the values of k_H via Marcus theory. From initial k_H values for reactions with radical **6**, new k_H values were calculated for increasingly exergonic reactions until the derived k_r values from the three trapping agents agreed with one another and an extrapolated value of k_r from Tempo trapping of **1**. The results suggest that hydrogen atom transfer reactions with **1** were about 3 kcal/mol more exergonic than reactions with **6**. Arrhenius functions for ring opening of **1** averaged log (k_s/s^{-1}) = 13.0 − 5.2/2.3RT; the value of k_r at 25 °C is 1.5 × 10^9 s^{-1}. Trapping studies of **1** and **6** with 2,6-dimethylthiophenol indicated that no special steric effects were present in hydrogen atom transfers to **1**. However, highly stereoselective trapping of **1** was observed in reactions with ArSD with *endo*-bicyclo[2.1.0]pentane-*2-d* predominating, and the rate constant for decarboxylation of the *endo*-bicyclo[2.1.0]pentane-2-carboxy radical (*endo*-**3**) at −78 °C apparently was greater than that for decarboxylation of *exo*-**3**. The stereochemical results are ascribed to a stereoelectronic effect between the C1–C4 bond and *endo*-C2–X bonds of bicyclo[2.1.0]pentanes that weakens *endo*-C2–X bonds.

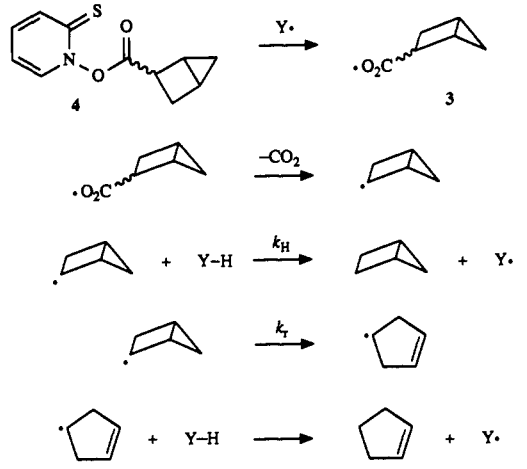
The ring opening of the bicyclo[2.1.0]pent-2-yl radical (**1**) to the cyclopent-3-enyl radical (**2**)[1] was shown to be exceptionally fast by Jamieson et al.,[1] who were unable to observe an ESR spectrum for radical **1** at temperatures as low as −160 °C. On

0002-7863/91/1513-949$02.50/0

Scheme I



Scheme II



the basis of a lower limit of 100 s^{-1} for ring opening at this temperature and an expected log A term in the Arrhenius function of 13,[2] the rate constant for ring opening at 25 °C would exceed 6×10^8 s^{-1}. Recently, Bowry et al.[5] reported a calibration of the ring opening of **1** at 37 °C using trapping by 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (Tempo) as a competition reaction; they[5] determined a rate constant of $k_r = 2.4 \times 10^9$ s^{-1} at 37 °C, which would place the ring opening of radical **1** among the fastest calibrated radical rearrangements that involve bond breaking or bond making. The latter work was in part a response to an impressive study of cytochrome P-450 oxidation mechanisms reported by Ortiz de Montellano and Stearns,[6] who found that P-450 oxidation of bicyclo[2.1.0]pentane gave radical **1** that ring opened to **2** in competition with trapping (Scheme I). By combining the product distribution in the P-450 study with the value for k_r, Ingold et al.[5] calculated a pseudo-first-order rate constant for the "oxygen rebound" step in the P-450 oxidation of $k_{OH} = 2 \times 10^{10}$ s^{-1} at 37 °C. The probe study[6] of the P-450 oxidation also provided other interesting results that were interpreted as evidence of stereochemical control in the oxidation reaction by the enzyme active site; labeling studies showed that the *endo*-hydrogen at C-2 of bicyclo[2.1.0]pentane was selectively abstracted, and the only bicyclic alcohol detected was the *endo*-alcohol shown in Scheme I.

The paper by Ortiz de Montellano and Stearns also directed our attention to the ring opening reaction of radical **1**. In this work, we report studies of competition reactions between the ring opening and trapping of **1** by hydrogen atom donors via the "PTOC-thiol" method in Scheme II. Relative rate constants for ring opening and trapping were measured over a wide temperature range, and an Arrhenius function for ring opening of **1** was determined. Radical **1** was found to be more reactive with hydrogen atom donors than a simple alkyl radical, but, despite this reactivity, highly stereoselective endo trapping of **1** by deuterated thiols was observed. In addition, the rate constant for decarboxylation of the *endo*-carboxy radical **3** at −78 °C apparently was greater than that for the *exo*-carboxy radical. These observations suggest that a stereoelectronic effect weakens the *endo*-C2 bonds of bicyclo[2.1.0]pentane and that the unique properties of this system were at least partially responsible for the stereochemical results found in the P-450 oxidation study.

Results

The kinetic competition method used in this study (Scheme II) was recently described.[4] Bicyclo[2.1.0]pent-2-yl radical (**1**) was produced in a radical chain reaction employing a Barton PTOC ester[7] (**4**) as the radical precursor. Addition of radical Y· to **4** with subsequent or concomitant cleavage of the N–O bond gave carboxy radicals **3** that decarboxylated to give **1**. Radical **1** was either trapped by a hydrogen atom donor (Y–H) or ring opened to radical **2** (C-1–C-4 cleavage), which also was subsequently trapped by Y–H. In principle, ring opening of **1** by C-1–C-5 cleavage to give the (2-cyclobutenyl)methyl radical could occur, but this mode of ring opening was not observed previously[1,5] or in this work; GC product analyses indicated that bicyclo[2.1.0]pentane and cyclopentene were the only low-weight products.

The PTOC-thiol competition method was described with thiophenol as the trapping agent Y–H.[4] However, several hydrogen atom donors can be used in the method with the only limitation being that radical Y· must successfully propagate a radical chain reaction by adding to the PTOC precursor. The method has recently been used with *t*-BuSH as the donor.[8] The phenylselenyl radical (PhSe·) is known to add rapidly to PTOC precursors,[9] and we have also employed PhSeH as a trapping agent in this work.

The PTOC precursors **4** were prepared by a standard method[10] from the corresponding acids. For most of our studies, a 60:40 mixture of *endo*- and *exo*-**4** was employed as the radical precursor. Upon decarboxylation of *endo*- and *exo*-**3**, the first formed radicals **1** might be distinct. However, these radicals should rapidly lead to the same radical (or mixture of radicals). This expectation was confirmed experimentally when isomerically pure samples of *endo*- and *exo*-**4** were used in some studies. Although the rates of decarboxylation of *endo*- and *exo*-**3** apparently are different (see below), the product distributions from reactions of **1** were not a function of the identity of the precursor.

The stability of the hydrocarbon products to the reaction conditions was tested. We were most interested in establishing that a thiol addition reaction did not consume some of the cyclopentene. The yields of hydrocarbon products typically were very high (usually greater than 90%), but traces of high-weight compounds were detected by GC–mass spectral analysis of some product mixtures from reactions of **4** with PhSH. These compounds most likely arose from radical–radical coupling reactions on the basis of two observations. First, when reaction mixtures were allowed to stand for extended periods, the yields of low-weight hydrocarbon products remained high. Second, a reaction of the PTOC precursor from lauric acid (precursor to the undecyl

(1) Jamieson, C.; Walton, J. C.; Ingold, K. U. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1366.
(2) For the rigid radical **1**, ring opening is expected to have $\Delta S^{\ddagger} = 0$, which gives a log A term of 13.1 at 25 °C.[3] Ring opening of the cyclopropylcarbinyl radical has log A = 13.15,[4] and correction for the degenerate modes for cyclopropylcarbinyl ring opening gives a log A value of 12.85 for cleavage of one of the bonds.
(3) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.
(4) Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275.
(5) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1989**, *111*, 1927.
(6) Ortiz de Montellano, P. R.; Stearns, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 3415.
(7) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901.
(8) (a) Newcomb, M.; Park, S. U. *J. Am. Chem. Soc.* **1986**, *108*, 4132. (b) Newcomb, M.; Glenn, A. G.; Manek, M. B. *J. Org. Chem.* **1989**, *54*, 4603.
(9) Barton, D. H. R.; Bridon, D.; Zard, S. Z. *Tetrahedron Lett.* **1984**, *25*, 5777.
(10) Barton et al.[7] have reported several procedures for the preparation of PTOC esters. The recommended method for α-branched carboxylic acids, reaction of the acid with the salt prepared from *N*-hydroxypyridine-2-thione and phosgene, was used for the synthesis of PTOC **4**.

Table I. Results of Trapping Studies with Thiols

thiol	temp, °C	$[Y-H]_m$,[a] M	R/U[b]	k_r/k_H[c]
t-BuSH	26	3.14	11.45	36.0
	0.5	2.00	9.00	18.0
		2.94	5.82	17.1
	−10	0.90	11.95	10.8
	−20	0.88	8.09	7.12
		1.36	4.37	5.94
	−45	0.48	5.56	2.67
		0.90	2.94	2.65
	−60	0.38	4.38	1.66
	−73	0.48	2.38	1.14
		0.90	1.07	0.96
PhSH	50	1.02	4.09	4.17
	48	1.90	1.66	3.15
	38	1.02	2.85	2.90
	28	0.97	2.34	2.27
	26	2.14	1.15	2.46
		1.03	2.43	2.51
	19.5	3.91	0.46	1.78
		2.99	0.61	1.81
		2.02	0.96	1.93
		0.64	3.06	1.96
	5	1.01	1.79	1.81
	1	1.98	0.56	1.12[d]
		0.98	1.18	1.15[d]
	0	1.98	0.64	1.26
		0.98	1.24	1.22
		1.94	0.63	1.22[e]
		0.94	1.38	1.30[e]
	−20.5	1.02	0.83	0.85
	−21.5	1.48	0.54	0.80
		0.98	0.82	0.80
		0.47	1.71	0.80
	−44	1.02	0.48	0.49
	−78	2.44	0.102	0.249
		1.42	0.154	0.219
		0.48	0.512	0.246
PhSD	19.5	2.95	0.99	2.92
		1.97	1.73	3.41
		0.98	3.54	3.47

[a] Average concentration of trapping agent. [b] Observed ratio of cyclopentene to bicyclo[2.1.0]pentane. [c] From eq 1. [d] The precursor was *endo*-**4**. [e] The precursor was *exo*-**4**.

radical) with 10 equiv of PhSH was conducted at 30 °C in a THF solution that contained 1 equiv of cyclopentene and an internal standard; GC and GC–mass spectral analyses of the reaction mixture after 24 h indicated quantitative formation of undecane, quantitative return of cyclopentene, and no evidence of a product from addition of PhSH to cyclopentene.

Thiol Trapping Reactions. When precursor **4** was allowed to react in the presence of *t*-BuSH in solvent THF, bicyclo[2.1.0]pentane and cyclopentene were formed in high yields as determined by GC. At ambient temperature, ring opening of **1** was much faster than trapping by *t*-BuSH even at high concentrations of the thiol, but as the reaction temperature was reduced, the trapping reaction became increasingly competitive. Table I contains the product ratios obtained in trapping reactions at various temperatures.

In the *t*-BuSH trapping studies, the concentration of thiol was much greater than that of the radical precursor, and the trapping reaction is adequately represented as a pseudo-first-order process with a pseudo-first-order rate constant (k') equal to $k_H[Y-H]_m$, where k_H is the second-order rate constant and $[Y-H]_m$ is the average concentration of hydrogen atom donor. The ratio of the rate constant for ring opening of **1** (k_r) to that for hydrogen atom trapping of **1** (k_H) is given by

$$k_r/k_H = [Y-H]_m[R]/[U] \quad (1)$$

where [R] and [U] are the observed yields of the rearranged and unrearranged products, respectively. The ratios of rate constants from eq 1 are included in Table I.

A similar set of studies was conducted with PhSH as the trapping agent for radical **1**, and the results are also contained in Table I. At the higher reaction temperatures, the two hydrocarbon products were formed nearly quantitatively, but a small amount of carboxy radicals **3** was trapped by PhSH at lower reaction temperatures (see below). PhSH was employed in large excess in these reactions, so eq 1 was again used to calculate the ratio of rate constants k_r/k_H.

Table II. Trapping Results with Thiol **5** at 0.4 °C

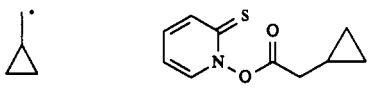
radical	$[RSH]_m$[a], M	R/U[b]	k_r/k_H[c]
6	0.51	1.87	0.95
	1.10	0.85	0.94
	1.45	0.69	1.00
1	0.71	5.06	3.59
	1.47	2.56	3.76
	2.13	1.80	3.83

[a] Average concentration of thiol **5**. [b] Observed ratio of 1-butene to methylcyclopropane for radical **6** and cyclopentene to bicyclo[2.1.0]pentane for radical **1**. [c] From eq 1.

A potential effect of the identity of the immediate radical precursor was tested in the PhSH trapping reactions. Samples of isomerically pure *endo*- and *exo*-PTOC ester **4** were prepared and allowed to react in the presence of PhSH at ca. 0 °C. The values for k_r/k_H for the isomerically pure precursors and for the mixture of precursors were essentially the same (Table I). This shows that trapping by PhSH was slower than equilibration of the radicals first formed in the decarboxylation reactions of carboxy radicals **3**.

A kinetic isotope effect for thiophenol trapping at 19.5 °C was determined. Three trapping reactions with PhSD were conducted at this temperature (Table I). A plot of [R]/[U] against $1/[PhSD]_m$ had a slope of 3.69 M. For the four reactions conducted at 19.5 °C with PhSH, the corresponding plot had a slope of 1.99 M. Dividing the former by the latter gives a value of k_H/k_D of 1.85. This small kinetic isotope effect is consistent with slight bond breaking in the transition state for the highly exergonic hydrogen atom transfer reaction.

Highly stereoselective trapping of radical **1** by deuterated thiols (see below) suggested that tests for steric effects in the thiol trapping reactions would be useful. 2,6-Dimethylthiophenol (**5**) was selected as a hindered trapping agent, and PTOC ester **4** was allowed to react in the presence of this thiol at 0.4 °C. To calibrate the potential steric effect, thiol **5** was also used to trap the cyclopropylcarbinyl radical (**6**) produced from the corresponding PTOC ester **7**.[4] The results are given in Table II. The average



6 **7**

value of k_r/k_H for trapping radical **1** by thiol **5** at 0.4 °C was 3.7 M, which is about 3.1 times the value found for trapping **1** by PhSH at this temperature; in other words, trapping of **1** by thiol **5** was 0.32 times as fast as trapping by PhSH. However, thiol **5** also reacted less rapidly with radical 6 than did PhSH. From the data in Table II and the reported[4] relative rate constants for ring opening of **6** and trapping by PhSH, thiol **5** trapped radical **6** 0.37 times as fast as did PhSH. Therefore, hindered thiol **5** apparently does not experience a significantly greater steric effect in trapping radical **1** than it does in trapping radical 6, and we can assume that no special steric effects come into play in trapping radical **1** by other, less hindered hydrogen atom donors.

Benzeneselenol Trapping Reactions. As noted above, PhSeH can also be employed in indirect kinetic measurements with PTOC radical precursors. PTOC ester **4** was allowed to react in the presence of PhSeH at various temperatures. High yields of bicyclo[2.1.0]pentane and cyclopentene were found for reactions conducted at temperatures between 0 and 50 °C. As with PhSH, PhSeH partially trapped carboxy radicals **3** in competition with the decarboxylation reactions at low temperatures.

An excess of PhSeH was used in all of the trapping studies, but due to the large rate constant for hydrogen atom transfer from the selenol,[11] low concentrations of PhSeH were employed. At

Table III. PhSeH Trapping Results

temp, °C	$[Y-H]_i$[a]	$[Y-H]_f$[b]	R/U[c]	k_r/k_H[d]
50	0.120	0.098	5.473	0.595
38	0.340	0.300	1.427	0.457
30	0.123	0.097	3.218	0.354
	0.226	0.200	1.509	0.321
20	0.080	0.040	4.809	0.286
	0.168	0.128	2.255	0.260
10	0.096	0.070	2.255	0.186
0	0.065	0.035	2.973	0.148
	0.080	0.050	2.127	0.138
	0.130	0.100	1.191	0.137
	0.168	0.138	0.900	0.138
	0.195	0.165	0.773	0.139
	0.240	0.210	0.655	0.147
	0.260	0.230	0.555	0.136
	0.520	0.490	0.345	0.174
	1.320	1.290	0.100	0.130
−45	0.126	0.096	0.687	0.076
−78	0.200	0.175	0.211	0.040

[a] Initial concentration of PhSeH. [b] Final concentration of PhSeH. [c] Observed ratio of cyclopentene to bicyclo[2.1.0]pentane. [d] From eq 2.

low concentrations, the approximation in eq 1, which employs the mean concentration of trapping agent, would introduce a small error in the values of k_r/k_H. Therefore, the relative rate constants for the PhSeH reactions were calculated from eq 2, which results from integration of the expression obtained by division of the rate law for rearrangement (by use of a steady-state approximation for the rearranged radical) by that for trapping. In eq 2, $[Y-H]_0$

$$[R] = k_r/k_H\{\ln([Y-H]_0 + k_r/k_H) - \ln([Y-H]_f + k_r/k_H)\} \quad (2)$$

is the initial and $[Y-H]_f$ the final concentration of trapping agent and [R] is the observed yield of rearranged product, cyclopentene. Table III contains the results of the PhSeH trapping studies.

Double-Competition Studies. Under Discussion, we will show that rate constants for trapping the cyclopropylcarbinyl radical (**6**) by the hydrogen atom donors are not appropriate basis rate constants for trapping radical **1**. Specifically, when the experimental values of k_r/k_H for radical **1** are multiplied by values of k_H for the cyclopropylcarbinyl radical trapping, a different value of k_r for ring opening of radical **1** is calculated for each donor. To verify that unexpected errors from independent relative kinetic measurements did not lead to the above results, we performed two experiments in which both radicals were produced in the presence of a hydrogen donor.

A mixture of PTOC esters **4** and **7** in THF was allowed to react at 0 °C in the presence of PhSH and in the presence of PhSeH. Our GC analytical method permitted resolution of all of the hydrocarbon products formed in the two reactions. From the product yields, the values of k_r/k_H were calculated for both radicals with each donor via eq 1. The concentration of PhSH employed was 15 times the sum of the concentrations of **4** and **7**, and, thus, it was effectively constant during the reaction. The concentration of PhSeH employed was only 2.6 times the sum of the concentrations of **4** and **7**, and a minor concentration effect would be expected in the PhSeH study. However, one would expect little if any discrimination in the additions of PhSe• to PTOC precursors **4** and **7**, and it is reasonable to assume that radicals **1** and **6** were formed at comparable rates throughout the reaction and experienced the same effective concentration of donor.

From the experiment conducted with PhSH, k_r/k_H for radical **1** was 1.39 M and k_r/k_H for radical **6** was 0.37 M. If trapping of both radicals had the same rate constant, then radical **1** rearranged 3.8 times faster than radical **6**. However, from the PhSeH experiment, k_r/k_H for radical **1** was 0.13 M and k_r/k_H for radical **6** was 0.015 M; these values suggest that radical **1** rearranged 8.7 times faster than radical **6**. This inconsistency requires that the values of k_H for reaction of at least one of the donors with radicals **1** and **6** are not equal.

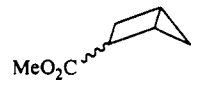
Table IV. Results from Deuterium Trapping Studies

donor	temp, °C	endo/exo[a]
PhSD	−78	95:5
		94:6
		95:5
		93:7[b]
		93:7[c]
	1.5	93:7[d]
$2,6\text{-}Me_2C_6H_3SD$	−50	94:6[e]
PhSeD	0	66:34[f]

[a] Observed ratio of *endo*- to *exo*-bicyclo[2.1.0]pentane-2-*d*. [b] The precursor was *endo*-**4**. [c] The precursor was *exo*-**4**. [d] 37% cyclopentene-4-*d* was observed. [e] 40% cyclopentene-4-*d* was observed. [f] The signal from cyclopentene-4-*d* was not adequately resolved from that of (natural abundance) THF to permit quantitation by ^2H NMR spectroscopy; GC analysis of the reaction mixture showed a 1:2 ratio of bicyclo[2.1.0]pentane to cyclopentene.

Decarboxylation Reactions. At low reaction temperatures, both PhSH and PhSeH trapped a small amount of carboxy radicals **3** in competition with the decarboxylation step in Scheme II. The partial trapping of the carboxy radicals did not interfere with a kinetic analysis of the relative rates of ring opening and trapping of radical **1** because, as we have noted, the identity of the precursor carboxy radical was shown to be unimportant. However, in the context of stereoelectronic effects in reactions of the system (see Discussion), it is noteworthy that *endo*-**3** apparently decarboxylated faster than *exo*-**3**.

For three reactions conducted at −78 °C with the ca. 60:40 (endo:exo) mixture of PTOC **4**, the acidic products were converted to methyl esters **8** by reaction with diazomethane, and the methyl esters were analyzed by GC; authentic samples of esters **8** permitted an unequivocal identification of the products. The experimental design did not permit a direct quantitation of the total amounts of the esters **8**, but the relative amounts of *endo*- and *exo*-**8** were readily determined. In these reactions, the ratios of *endo*-**8** to *exo*-**8** were 0.45 (0.48 M PhSH), 0.33 (0.98 M PhSH), and 0.30 (0.18 M PhSeH). If one assumes that the rate constants for reactions of the *endo*- and *exo*-carboxy radicals **3** with a given donor are approximately equal, then the formation of acidic products enriched in the *exo*-acid requires that the rate constant for decarboxylation of *endo*-**3** was greater than that for decarboxylation of *exo*-**3**.



8

Labeling Studies in Trapping Reactions. On the basis of the relatively small kinetic isotope effect in the PhSH trapping reaction at 19.5 °C, one could anticipate that highly efficient trapping of radical **1** at low temperatures was possible with PhSD. Several trapping reactions were conducted with deuterated donors, and the product mixtures were analyzed by ^2H NMR spectroscopy. The chemical shifts for the *endo*- and *exo*-protons on C-2 of bicyclo[2.1.0]pentane differ by 0.8 ppm, and the signals were readily differentiated by ^2H NMR at 29 MHz both from one another and from the signal for the C-4 protons on cyclopentene. Chemical shift assignments for bicyclo[2.1.0]pentane were known,[13] and we confirmed the assignments by observing long-range W-coupling between the *exo*-protons on C-2 and C-5 in ^1H NMR decoupling experiments at 200 MHz. Most of the labeling studies were conducted at low temperatures to prevent significant ring opening of **1**, and a portion of the carboxy radicals **3** was trapped before decarboxylation. We could not determine the amount of acids formed by trapping because RCO_2D rapidly exchanged with the large amount of Y–D in the sample, but

(11) The measurement of k_H values for PhSeH is a subject of current interest in our group. Preliminary measurements[12] show that at 0 °C radical **6** is trapped by PhSeH 20 times faster than it is trapped by PhSH.

(12) Newcomb, M.; Manek, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 9662.

(13) Roth, W. R.; Martin, M. *Liebigs Ann. Chem.* **1967**, *702*, 1.

Table V. Diffusion Coefficients[a]

temp, °C	D_{THF}[b]	D'_{THF}[c]	D'_{PhSH}[c]	D''_{THF}[d]	D''_{PhSH}[d]
−10	2.15	1.81	1.27	1.47	1.39
0	2.49	1.96	1.39	1.71	1.52
10	3.07	2.33	1.61	1.97	1.79
22	3.74	2.87	2.07	2.35	2.10
35	4.44	3.32	2.52		

[a] Diffusional coefficients in units of 10^{-5} cm^2 s^{-1}. [b] Neat THF. [c] 1 M PhSH in THF. [d] 2 M PhSH in THF.

neither the presence of RCO_2D nor our ignorance of the extent of decarboxylation interfered with the analysis. The results of the deuterium labeling studies are collected in Table IV.

Highly diastereoselective trapping by PhSD was observed with the endo deuterated bicyclo[2.1.0]pentane predominating. At the level of selectivity observed, the accuracy of the integration of the signal from the exo deuterated species limited the accuracy in the ratio of the products, but it is apparent that the ratio of $k_{H(endo)}/k_{H(exo)}$ was about 16 at −78 °C. In two of the studies conducted at −78 °C, the isomerically pure samples of *endo*- and *exo*-PTOC ester **4** were used; as with the kinetic studies at ca. 0 °C, the product distribution was not a function of the identity of the precursor carboxy radical, again showing that equilibration of radical **1** was complete before trapping. One reaction conducted with 2,6-dimethylthiophenol-*S*-*d* (**5**-*d*) at −50 °C gave a similarly high ratio of endo to exo trapping consistent with the conclusion from the kinetic studies with the hindered thiol **5** that no unusual steric effects were present. A trapping reaction with PhSeD at 0 °C also gave predominantly endo substituted product but with less selectivity than observed in the other trapping reactions.

The results of the PhSD trapping reaction at 1.5 °C permitted a check on the experimental method. A crude value for k_r/k_D of 1.9 M was calculated from the observation that cyclopentene-4-*d* comprised 37% of the hydrocarbons. From Table I, the average k_r/k_H value at ca. 0 °C for PhSH trapping of **1** was 1.3 M. Combining these values gives an approximate k_H/k_D of 1.5 that is in reasonable agreement with the more precise kinetic determination at 19.5 °C.

Diffusion Effects. Under Discussion, we will show that second-order trapping reactions of radical **1** are faster than analogous trapping reactions of the cyclopropylcarbinyl radical. With exceptionally fast second-order reactions, one must be concerned with the possibility that the reactions can become partially diffusion controlled.[14] Therefore, we have attempted to determine approximate rate constants for diffusion in our systems.

The diffusion rate constant (k_{diff}) for reaction of entities A and B can be calculated from the von Smoluchowski equation (eq 3),

$$k_{diff} = 4\pi N(D_A + D_B)d_{AB} \quad (3)$$

where N is Avogadro's number, D_x is the diffusional coefficient for each reacting species, and d_{AB} is the distance between the species at which the reaction will occur.[16] Diffusional coefficients (D) for THF and THF solutions containing PhSH were measured directly by the pulse gradient spin echo (PGSE) NMR method.[17] The field gradient established by the homospoil pulse in our instrument was calibrated with absolute methanol for which the self-diffusion coefficient is known.[18a] Unfortunately, due to instrumental design limitations, thermal gradients resulting in convective bulk mixing precluded studies at temperatures that were not close to ambient, but apparently reliable results were obtained in the temperature range −10 to 35 °C. Table V contains the experimentally determined values of D.

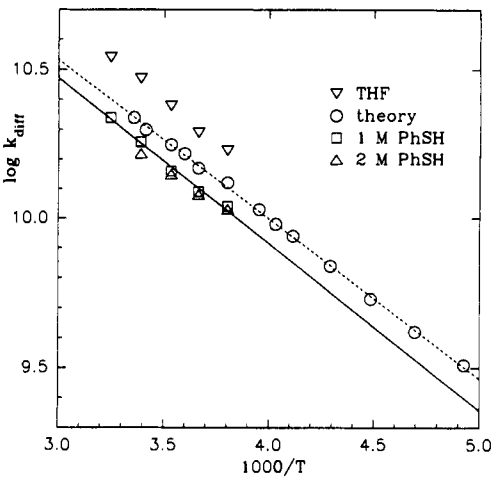


Figure 1. Diffusional rate constants for reactions of **1** with PhSH in 1 and 2 M PhSH solutions in THF and for self-diffusion of THF in THF and theoretical k_{diff} in THF based on reported viscosities. The solid line is for the 1 M PhSH data. The dashed line is for the theoretical values.

Diffusional coefficients for radical **1** were estimated in the following manner. Cyclopentene (CP) was taken as a model of **1**, and D_{CP} values at 22 °C for 1, 2, 5, and 9.8 M solutions of CP in THF were measured. A plot of D_{CP} versus [CP] was extrapolated to [CP] = 0.0 M to obtain D_{CP} at infinite dilution in THF, which was found to be equal to $0.82D_{THF}$. The diffusion coefficient for radical **1** was then taken to be equal to $0.82D_{THF}$ for each solution and temperature measured in Table V.

Diffusion rate constants were calculated for reactions of PhSH with radical **1** via eq 3. We made the approximation that d_{AB} is the sum of the radii of the reacting species.[15b] We further approximated the reacting entities as spheres which permits a calculation of the molecular volume (and thus the radius) by the van der Waals increment method described by Bondi.[19] With the value for D for radical **1** taken to be equal to $0.82D_{THF}$ and the experimental values of D for PhSH, k_{diff} values for reactions containing 1 and 2 M PhSH in THF were calculated; these are shown graphically in Figure 1. Also shown in Figure 1 are values for self-diffusion between two molecules of THF in neat THF and the theoretical values of k_{diff} for reaction of infinitely dilute species in THF calculated with D values resulting from measured viscosities of THF.[20]

Over a reasonably narrow temperature range, the diffusional rate constant behaves as if it is a typical second-order rate constant, and values for an apparent log A and E_a can be calculated. For the various sets of data in Figure 1, the apparent activation parameters are similar. The results from measurements in 1 M PhSH gave an apparent log A = 12.14 and E_a = 2.54 kcal/mol, and these values were used below for calculations of k_{diff}.

(14) The effect of diffusion on the rate constant for a second-order reaction in the encounter complex model is shown in eq i, where k_{obs} is the observed

$$k_{obs} = k_{chem}k_{diff}(k_{diff} + k_{chem})^{-1} \quad (i)$$

rate constant, k_{chem} is the rate constant for the chemical reaction, and k_{diff} is the diffusion rate constant.[15]

(15) (a) Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987; p 216. (b) Calef, D. F.; Deutch, J. M. *Annu. Rev. Phys. Chem.* **1983**, *34*, 493.

(16) Rice, S. A. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Compton, R. G., Eds.; Elsevier: Amsterdam, 1985; Vol. 25, pp 7–21.

(17) (a) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288. (b) Hahn, E. L. *Phys. Rev.* **1950**, *80*, 580. (c) James, T. L.; McDonald, G. G. *J. Magn. Reson.* **1973**, *11*, 56. (d) Pratum, T. *Magn. Moments* **1989**, *3*, 6.

(18) (a) Sandhu, H. S. *J. Magn. Reson.* **1975**, *17*, 34. (b) Stilbs, P.; Moseley, M. E. *Chem. Scr.* **1980**, *15*, 176.

(19) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. Edwards, J. T. *J. Chem. Educ.* **1970**, *47*, 261.

(20) Theoretical values for D in THF were calculated from the modified Stokes–Einstein relationship for slip boundary conditions (eq ii), where k_B is

$$D = k_BT/4\pi\eta r_x \quad (ii)$$

Bolizmann's constant, η is the dynamic viscosity of the solvent, and r_x is the radius of species X.[21] Known values of η for THF[22] were used, and the radii were approximated from molecular volumes determined by the method of Bondi.[19]

(21) Reference 16, p 45. Dullien, F. A. L. *Trans. Faraday Soc.* **1963**, *59*, 856.

(22) Carvajak, C.; Tölle, K. J.; Smid, J.; Szwarc, M. *J. Am. Chem. Soc.* **1965**, *87*, 5548.

Discussion

Structure of Bicyclo[2.1.0]pent-2-yl Radical. The structure of radical **1** is a factor that our results cannot address directly. The cyclopropyl radical is a rapidly interconverting pair of σ-radicals,[23] whereas the cyclobutyl radical is most likely a planar π-radical.[24] One might anticipate that radical **1** is an unsymmetrical π-radical, but the rapid ring opening of **1** has thus far precluded an ESR study of the species.[1]

The structure of **1** will have a bearing on the kinetic and stereochemical analyses. If **1** is a π-radical, then one needs only to consider one ring opening reaction and two distinct trapping reactions. Alternatively, if **1** is a pair of σ-radicals, then there are two ring opening reactions and two trapping reactions as well as a reaction that interconverts the pair of radicals. If the latter model is correct, the radical interconversion reaction is almost certainly very fast on the basis of the fact that cyclopropyl radicals invert[23a] with rate constants of 10^{11}–10^{12} s^{-1} at 71 °C as well as our observation that the identity of the precursor to **1** was not important in kinetic and labeling studies. Accordingly, a pair of σ-type radicals **1** would behave as a single species in the competitions between ring opening and trapping but would not necessarily give rise to a linear Arrhenius function for ring opening. Further, because there must be two distinct trapping reactions regardless of the structure of **1**, the trapping kinetics might not be described by a linear Arrhenius function in either case. In the following discussion, we have assumed that **1** is an unsymmetrical π-radical.

Stereoselective Reactions. The highly stereoselective trapping of radical **1** by deuterated thiols was surprising. The transition states for endo and exo trapping of **1** cannot be identical, but one might have expected that the two transition states would have had quite similar activation parameters in light of the highly exergonic nature of the trapping reaction and the fact that the same products are formed in the two processes. In fact, from a simple consideration of radical **1**, the only difference in the two transition states we initially envisioned was a potential steric effect that inhibited the endo trapping reaction. Others have also assumed that the transition states for endo and exo trapping of radical **1** would be similar.[5,6]

The kinetic and labeling studies with 2,6-dimethylthiophenol indicate that steric effects in the hydrogen-transfer reactions to radical **1** are inconsequential, and the results with the isomerically pure samples of PTOC precursor **4** show that the identity of the radical precursor is unimportant. Therefore, the observed stereoselective trapping by PhSD must be ascribed to differences in the transition-state energies for the two trapping reactions, and these differences must primarily reflect differences in the strengths of the *endo*- and *exo*-C-2 carbon–hydrogen bonds in bicyclo[2.1.0]pentane. For PhSD trapping at −78 °C, endo trapping was favored with a $\Delta\Delta G^{\ddagger}$ of about 1.1 kcal/mol. On the basis of microscopic reversibility, the *endo*-C-2 hydrogen in bicyclo[2.1.0]pentane must also be abstracted by PhS• more readily than the *exo*-C-2 hydrogen in a process favored by the same amount. The observed small k_H/k_D for reaction of radical **1** with PhSH at 19.5 °C shows that the C–H bond is either slightly or greatly formed in the transition state for hydrogen transfer, but, on the basis of the highly exergonic nature of the reaction (see below), the C–H bond is most likely only slightly formed. The observed $\Delta\Delta G^{\ddagger}$ in the PhSD reactions with **1** undoubtedly reflects a significant difference in the bond strengths of the *endo*- and *exo*-hydrogens in the precursor hydrocarbon.

The C–H bond energy differences at C-2 in bicyclo[2.1.0]-pentane almost certainly result from a stereoelectronic effect involving conjugation of the C-1–C-4 bond with the *endo*-C-2–H antibonding orbital. High-level calculations of the molecule by Wiberg et al.[25] showed that the C-1–C-4 bond is bent above the plane defined by C-1–C-2–C-3 and that the *endo*-C-2–H bond is 0.0022 Å longer than the *exo*-C-2–H bond reflecting the weaker endo bond. One can roughly estimate that the difference in bond lengths corresponds to a 2–3 kcal/mol energy difference in the two bonds.[26]

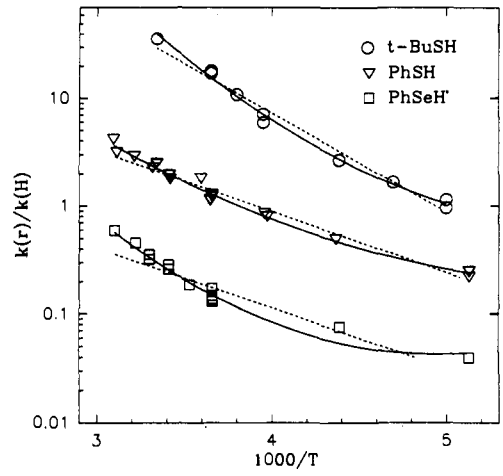


Figure 2. Ratios of rate constants (k_r/k_H) from Tables I and III. The dashed lines show the best linear fit of the data, and the solid lines show the best quadratic fit.

A stereoelectronic effect between the C-1–C-4 bond and an endo substituent at C-2 is also suggested by the apparent difference in rate constants for decarboxylation of *endo*- and *exo*-**3**. A faster decarboxylation of *endo*-**3** signals a weaker *endo*-C-2–CO_2• bond. Again, one would expect that the transition states for decarboxylation were achieved quite early in the reactions and that a small difference in activation energies reflects a significantly larger difference in the endo and exo bond energies.[28]

Nevertheless, one should note that the origins of selectivity in trapping reactions of radical **1** are complex. In the radical–radical coupling of **1** with the nitroxyl radical Tempo, the major product produced was the exo adduct.[5,30] In the radical coupling reaction, steric effects presumably are most important.

Irrespective of the origins of the preference for *endo*-C-2 hydrogen transfer trapping reactions, the results have an important implication for the cytochrome P-450 oxidation studies conducted by Ortiz de Montellano and Stearns.[6] In that work, selective abstraction of the *endo*-C-2 hydrogen and formation of only the *endo*-C-2 alcohol (Scheme I) were ascribed to constraints imposed by the enzyme active site. Our results cannot exclude stereochemical control by the enzyme, but they suggest that the special character of the bicyclo[2.1.0]pentane system and radical **1** was at least partially responsible for both of the stereoselective reactions observed in the P-450 study.

Rate Constants for Ring Opening of 1. The observed highly stereoselective reaction of **1** with PhSD simplifies a kinetic analysis of the PhSH data somewhat. Because endo trapping accounts for the major portion of these reactions, any differences in the

(23) Johnston, L. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1986**, *108*, 2343. Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625.
(24) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.
(25) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985, 1001.
(26) Generally, C–H bond lengths in related species correlate with the bond dissociation energies. For example, Wiberg's calculations[25] gave C–H bond lengths in cyclobutane that were 0.089 Å longer than those in cyclopropane. The C–H bond dissociation energy for cyclobutane is about 10 kcal/mol smaller than that for cyclopropane.[27a]
(27) (a) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (b) Griller, D.; Kanabus-Kaminska, J. M. *THEOCHEM* **1988**, *40*, 125. Bond dissociation values taken from these compilations might be systematically low by 2–3 kcal/mol; cf.: Tsang, W. *J. Am. Chem. Soc.* **1985**, *107*, 2872.
(28) A large stereoelectronic effect was observed in solvolyses of the 3,5-dinitrobenzoates of bicyclo[2.1.0]pentan-2-ol; at 50 °C, the rate constant for solvolysis of the endo isomer was about 7 orders of magnitude greater than that of the exo isomer.[29]
(29) Wiberg, K. B.; Williams, V. Z., Jr.; Friedrich, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 564.
(30) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.*, submitted for publication. We thank Dr. Ingold for communicating this information before publication.

activation parameters for endo and exo trapping should be manifested as minor perturbations of the activation parameters for endo trapping, and one can analyze the results in terms of a single trapping process. We have exercised that expediency in the following discussion.

The kinetic studies provide relative rate constants (k_r/k_H) for rearrangement and trapping of radical **1** by the various donors. If the rate constants for trapping are known, one can calculate rate constants for the rearrangement. However, inspection of the values of k_r/k_H reveals two significant problems. First, if one makes the assumption that the values of k_H for trapping **1** are equal to those for trapping simple primary radicals or the cyclopropylcarbinyl radical, then at a given temperature each trapping agent gives a different value for k_r and none of these values agrees with that extrapolated from the Tempo trapping study.[5] Second, when one plots the relative Arrhenius functions for rearrangement versus trapping, linear functions are not obtained (Figure 2). The former problem results because the rate constants for trapping simple primary radicals are not appropriate basis values for trapping radical **1**, and the latter problem results, at least in part, from the increasing importance of partially diffusion controlled trapping reactions at low reaction temperatures.

At the outset of this study, we had hoped that we could use values of k_H for reactions of our donors with primary radicals or with the cyclopropylcarbinyl radical (**6**) as the basis reactions for trapping radical **1**. This hope was based on the fact that, for both *t*-BuSH and PhSH trapping, there is good agreement between the rate constants for reactions with primary radicals and with **6**.[4,8b] However, the approximation for reactions of radical **1** is clearly not appropriate as one can see by focusing on the data collected at 0 °C. If the k_r/k_H values are multiplied by the known k_H values for reactions of the donors with cyclopropylcarbinyl radical[31] at 0 °C, then the *t*-BuSH results give a value for k_r for radical **1** of 1.04×10^8 s^{-1}, the PhSH results give a value of 1.25×10^8 s^{-1}, and the PhSeH results give a value of 2.65×10^8 s^{-1}.[32] Further, if one assumes that ring opening of radical **1** has the expected log A value of 13,[2] the Tempo results[5] at 37 °C lead to a predicted k_r at 0 °C of 7.7×10^8 s^{-1}. The variance of the four values of k_r over a factor of 8 far exceeds the expected experimental errors.

One can see that as the trapping reactions become more exergonic (*t*-BuSH < PhSH < PhSeH) there is a regular increase in the calculated values for k_r for radical **1**. This indicates that the trapping of radical **1** is more exergonic than the trapping of cyclopropylcarbinyl radical. On the basis of reactivity–selectivity principles, as the energy of the C–H bond formed in the hydrogen-transfer reaction becomes stronger (ΔG_0 for the reaction becomes increasingly negative), the rate constants for the trapping reactions will increase, and the slowest trapping reaction will increase most rapidly. The net effects of an increased C–H bond energy at C-2 of bicyclo[2.1.0]pentane in comparison to the methyl C–H bond energy of methylcyclopropane are that all of the calculated rate constants k_r will increase and the variance between the k_r values will narrow.

The above qualitative assessment can be evaluated in a semiquantitative manner by the use of Marcus theory.[33] The free energy of activation ($\Delta G^\ddagger$) for a reaction is given by eq 4, where

$$\Delta G^\ddagger = \Delta G^\ddagger_i + \Delta G_0/2 + (\Delta G_0)^2/16\Delta G^\ddagger_i \quad (4)$$

$$\Delta G^\ddagger_i = 0.5(\Delta G^\ddagger_A + \Delta G^\ddagger_B) \quad (5)$$

ΔG_0 is the free energy of the reaction and $\Delta G^\ddagger_i$ is the intrinsic free energy of activation of the reaction that is taken to be the average of the intrinsic free energies of the self-exchange reactions of the component species ($\Delta G^\ddagger_x$) according to eq 5. The self-exchange reactions in this case are the reactions of Y–H and R–H with Y$^\bullet$ and R$^\bullet$, respectively, for which $\Delta G_0 = 0$.

We have available values for $\Delta G^\ddagger$ for trapping the cyclopropylcarbinyl radical (**6**) by each donor,[31] and, with approximate values for ΔG_0, we can calculate the value of $\Delta G^\ddagger_i$ for each hydrogen donor reacting with **6** via eq 4. The free energies of the trapping reactions of 6 are not known, but we have approximated these values from estimations of the enthalpies of the reactions.[34] One should note that errors in the estimations of the free energies of reaction are compensated by the calculated intrinsic free energy term in eq 4. Table VI contains a summary of the values for reactions of our three hydrogen donors with cyclopropylcarbinyl radical at 0 °C.

In the next step of the analysis, we incrementally increased the bond dissociation energy (BDE) for the C–H bond formed in the hydrogen-transfer reaction and calculated new rate constants for the radical trapping reactions (k_H) for each donor. An increase in C–H BDE results in an equal (negative) increase in ΔG_0 for each reaction. As the C–H BDE increases and the radical becomes less stable, the self-exchange rate constant for the radical (reaction of R$^\bullet$ with R–H) might be expected to increase with the result that $\Delta G^\ddagger_i$ for the trapping reaction might decrease, but the amount of this change is not known. We have calculated values for two limiting cases. In one, we assumed that the self-exchange barrier for the radical was reduced by half of the increase in BDE; this results in a net reduction of $\Delta G^\ddagger_i$ by one-fourth of the increase

Table VI. Values Employed in Marcus Theory Calculations for Reactions at 0 °C

reaction	energy, kcal/mol ΔG_0[a]	$\Delta G^\ddagger$[b]	$\Delta G^\ddagger_i$[c]
6 + *t*-BuSH → *c*-$C_3H_5CH_3$ + *t*-BuS$^\bullet$	−7.0	7.48	10.69
6 + PhSH → *c*-$C_3H_5CH_3$ + PhS$^\bullet$	−16.5	5.92	12.85
6 + PhSeH → *c*-$C_3H_5CH_3$ + PhSe$^\bullet$	−29.0	4.30	15.38

[a] Taken to be equal to ΔH_0; see ref 23. [b] Calculated from the rate constants at 0 °C; see ref 31. [c] Calculated from eq 4.

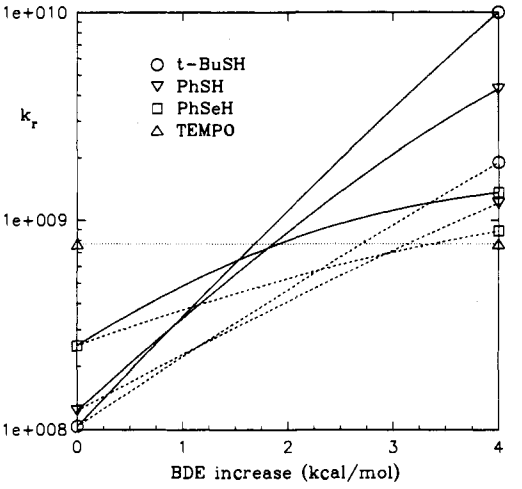


Figure 3. Results of Marcus theory calculations for k_r at 0 °C. The solid lines are for the limiting cases where $\Delta G^\ddagger_i$ was decreased by 25% of the increase in BDE; the dashed lines are for the limiting cases $\Delta G^\ddagger_i$ was held constant. The curvature (especially apparent in the PhSeH calculations) results from partial diffusion control of the trapping reactions. The value of k_r from Tempo trapping (dotted line) was extrapolated from results in ref 5; see text for details.

(31) The rate constants for reactions at 0 °C in THF of radical **6** with *t*-BuSH,[8b] PhSH,[4] and PhSeH[12] are 5.85×10^6, 1.05×10^8, and 2×10^9 M^{-1} s^{-1}, respectively.

(32) One can also evaluate a value of k_r for radical **1** at 0 °C from the 2,6-dimethylthiophenol (**5**) trapping results in Table II and the known rate constant for ring opening of radical **6**.[4] These results give a value of k_r of 1.4×10^8 s^{-1} if k_H for reactions of both radicals with thiol **5** are equal.

(33) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; pp 222–227.

(34) The BDE values used were the following: *c*-$C_3H_5CH_2$-H, 95 kcal/mol;[27,35] *t*-BuS-H, 88 kcal/mol;[3] PhSH, 78.5 kcal/mol.[36] We are unaware of a BDE for PhSeH; we assumed that the BDE difference between PhSeH and PhSH was equal to that between PhSH and PhOH[36] to give a BDE for PhSeH of 67 kcal/mol.

(35) Walton, J. C. *Magn. Reson. Chem.* **1987**, *25*, 998.

(36) Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229.

in BDE. In the other, we assumed that the self-exchange barrier for the radical was not reduced as the BDE increased.

From the new values of ΔG_0 and $\Delta G^{\ddagger}_i$, one can calculate a new value for k_H for each hydrogen donor. However, a final correction for k_H is still required. As the rate constant of the second-order hydrogen trapping reaction approaches the diffusion rate constant, the reaction will become partially diffusion controlled. Therefore, we further corrected the calculated values of k_H to account for partial diffusion control.[14] The value of k_{diff} at 0 °C of 1.2×10^{10} M^{-1} s^{-1} (which resulted from our diffusion studies) was employed.

Multiplication of the experimental values of k_r/k_H by the diffusion-corrected new rate constants for trapping gave new values for k_r. Figure 3 shows the results of the analysis. The ordinate lists the increase in BDE for the C–H bond formed in the reaction, and the calculated values for k_r for our two limiting cases are plotted. Figure 3 also contains a constant value for k_r resulting from an extrapolation of the results of the Tempo trapping study.[5] The Marcus analysis implies that the reactions are similar, so it would not be appropriate to apply the analysis for hydrogen atom transfer to the Tempo trapping results. More importantly, the rate constants for Tempo trappings (radical–radical coupling reactions) are quite insensitive to the stability of the radical, and the rate constant for Tempo trapping of a primary radical should provide a reasonably accurate approximation for the rate constant for Tempo trapping of a somewhat more reactive radical.[37]

The four values for k_r were in reasonable accord when the C–H BDE energy was increased to between 1.5 and 3.0 kcal/mol. The k_r value at which convergence occurred was the same for both limiting cases of $\Delta G^{\ddagger}_i$ behavior (and would also be the same for any case between the limits), and the only real difference in the limiting calculations was the increase in the BDE required to effect the convergence in k_r values. For the two limiting examples we calculated, the range of the k_r values was reduced to a factor of 1.2 (at 1.75 kcal/mol, varying $\Delta G^{\ddagger}_i$) and a factor of 1.3 (at 2.75 kcal/mol, constant $\Delta G^{\ddagger}_i$). The rate constant for ring opening of **1** at 0 °C is $7–8 \times 10^8$ s^{-1}. The rate constants for hydrogen transfer to radical **1** at 0 °C from *t*-BuSH, PhSH, and PhSeH are 4×10^7, 5×10^8, and 8×10^9 M^{-1} s^{-1}, respectively; we estimate an error range of 25% for the absolute values of the trapping rate constants, but the relative errors between the values will be smaller. The PhSH and PhSeH hydrogen atom transfer reactions are partially diffusion limited in THF; this has a small effect (ca. 5%) on $k_{H(PhSH)}$, but for PhSeH the observed rate constant is reduced to about 5×10^9 M^{-1} s^{-1}. The observed ratio of $k_{H(PhSeH)}$ to $k_{H(PhSH)}$ for reactions with radical **1** at 0 °C in THF should be about 10; this is in excellent agreement with the value of 11 that can be derived from the two double competition experiments performed at 0 °C and the value of 8.5 derived from the averages of the 0 °C results in Tables I and III.

As noted, the Marcus theory analysis will result in a convergence in the calculated values of k_r for **1** for a variety of models of the behavior of $\Delta G^{\ddagger}_i$; the selection of the extent of change in $\Delta G^{\ddagger}_x$ for radical **1** merely determines how rapidly the calculated k_r values converge as ΔG_0 becomes increasingly negative. This feature makes it difficult to select the proper ΔG_0 values for the trapping reactions and the BDE for bicyclo[2.1.0]pentane. However, we can use reported rate constants for reactions of PhSH with radicals as a guide for selection of the correct ΔG_0 value. Franz et al.[39] reported that primary alkyl radicals reacted with PhSH at 0 °C with values of $k_H = 8.5 \times 10^7$ M^{-1} s^{-1}. Ingold et al.[38b] have reported a rate constant for reaction of PhSH with cyclopropyl radical in benzene at 25 °C of $k_{obs} = 4.1 \times 10^9$ M^{-1} s^{-1}. Accounting for partial diffusion control in the cyclopropyl radical study,[40] the k_H for reaction of PhSH with cyclopropyl radical at 25 °C is 5.5×10^9 M^{-1} s^{-1}, which would give a k_H at 0 °C of about 5×10^9 M^{-1} s^{-1}.[42] When one applies the Marcus theory approach in the same manner as used for calculating k_H values for reactions with **1**, one finds that a k_H value of 8.5×10^7 M^{-1} s^{-1} would be increased to 5×10^9 M^{-1} s^{-1} when ΔG_0 becomes more negative by 3.0 kcal/mol (varying $\Delta G^{\ddagger}_i$) or by 7.2 kcal/mol (constant $\Delta G^{\ddagger}_i$). Because the C–H BDE of cyclopropane is about 6–8 kcal/mol greater than a primary C–H BDE,[38b] the latter approach (constant $\Delta G^{\ddagger}_i$) appears to be the better choice.

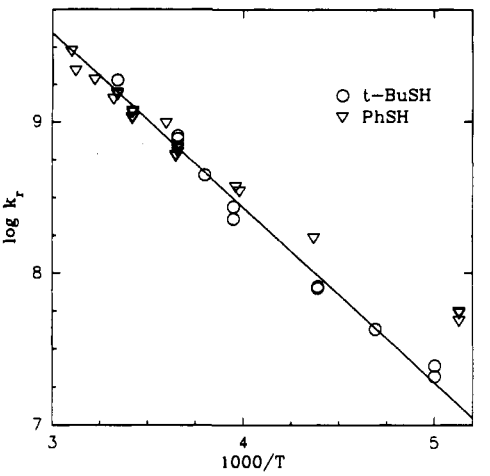


Figure 4. Derived k_r values for rearrangement of **1** from the *t*-BuSH and PhSH data in Table I. The line is eq 6.

From the above analysis, we conclude that the *endo*-C-2–H BDE of bicyclo[2.1.0]pentane is about 3 kcal/mol greater than the methyl C–H BDE in methylcyclopropane. From Walton's estimate[35] that the BDE of the methyl C–H in methylcyclopropane is similar to that of a tertiary C–H in an alkane (a tertiary C–H BDE is about 93 kcal/mol[27]), the *endo*-C-2–H BDE in bicyclo-[2.1.0]pentane would be about 96 kcal/mol. This value is in good agreement with observation[1] that at 50 °C *t*-BuO• reacted with bicyclo[2.1.0]pentane 0.62 times as fast as it reacted with cyclohexane (the C–H BDE of cyclohexane is 95.5 kcal/mol[27]) if one assumes that the reactions were activation limited rather than diffusion controlled. The value is similar to the C–H BDE in cyclobutane[27a] of 96.5 kcal/mol.[43]

The Marcus theory treatment can be extended over the entire temperature range of the studies. In Figure 4, we show the values of k_r calculated from the *t*-BuSH and PhSH results when the BDE for bicyclo[2.1.0]pentane was taken to be 2.75 kcal/mol greater than that for methylcyclopropane and $\Delta G^{\ddagger}_i$ was held constant. At relatively high temperatures, the donors provided k_r values that were very similar; for example, at 26 °C, the value from *t*-BuSH was 1.9×10^9 s^{-1}, the average from the PhSH results was 1.5×10^9 s^{-1}, and that interpolated from the 20 and 30 °C results with PhSeH (not included in Figure 4) was 1.8×10^9 s^{-1}.

The derived values of k_r for **1** from the *t*-BuSH data provide a nearly linear function and give the Arrhenius function in eq 6,

$$\log (k_r/s^{-1}) = 13.1(4) - 5.3(4)/\theta \quad (6)$$

$$\log (k_r/s^{-1}) = 12.9(2) - 5.1(2)/\theta \quad (7)$$

where θ is $2.3RT$ and the error limits given are 2σ for the last significant figure. When the results from the PhSH studies at and above 0 °C are combined with the *t*-BuSH results, the Ar-

(37) The rate constants for reactions of Tempo with several radical are similar.[38] In evaluating the expected rate constant for reaction of Tempo with a radical that is more reactive than a primary radical, it is important to note that Tempo reacts with the nonyl radical[38a] and the cyclopropyl radical[38b] with essentially the same rate constant.

(38) (a) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 1629. (b) Johnston, L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 4877.

(39) Franz, J. A.; Bushaw, B. A.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 268.

(40) An approximate value for $k_{diff(benzene-25°C)}$ is 1.6×10^{10} M^{-1} s^{-1}, which results from eq ii[20] and a value for η for benzene at 25 °C of 0.6028 cP.[41]

(41) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986; p 135.

(42) The log *A* value was assumed to be 10.5.

(43) There is a caveat. Franz et al.[39] have reported that 1°, 2°, and 3° radicals react with PhSH with similar rate constants, which is not consistent with the prediction from the Marcus theory calculations.

rhenius function in eq 7 is obtained. The log A terms are consistent with theory,[2] and the functions are in excellent agreement with the Arrhenius function recently determined by Tempo trapping studies; i.e., log (A/s^{-1}) = 13.05, E_a = 5.2 kcal/mol.[30] The calculated rate constants for k_r at 37 °C (2.3 and 2.0 × 10^9 s^{-1}) are in good agreement with the value of 2.4 × 10^9 s^{-1} determined in the Tempo trapping studies.[5,30] From eqs 6 and 7, the rate constant for ring opening of **1** at 25 °C is 1.5 × 10^9 s^{-1}, which is 16 times faster than the ring opening of the cyclopropylcarbinyl radical (**6**),[4] and the increased rate of reaction derives entirely from a reduction of the activation energy for opening of **1** relative to that for **6**.

At lower temperatures, the agreement in the derived values for k_r for radical **1** is poorer; for example, the values for k_r at −78 °C from the *t*-BuSH and PhSH results differ by a factor of 4. The results from each donor still show a curvature in the Arrhenius functions for k_r similar to that noted earlier in the k_r/k_H plots, although the curvature in the *t*-BuSH plot is only slight. An upward curvature at the low-temperature end of the k_r functions would result if our estimates for the values of k_{diff} at low temperatures were too large, and it is possible that the calculated k_H values for PhSH contain such errors. It is unlikely that the *t*-BuSH results reflect such an error, however, because the calculated value for $k_{H(t\text{-BuSH})}$ at −73 °C is 2 orders of magnitude smaller than the estimated k_{diff} at this temperature. We suspect that the poor agreement and curvature at low temperatures are due mainly to accumulated errors in the methods and the computational approximations that were aimed at obtaining consistent values at 0 °C. However, the behavior could result from the multiple reaction pathways for trapping **1**[44] or from the onset of other reaction channels for ring opening that we have not considered.[45]

Conclusion

The bicyclo[2.1.0]pent-2-yl radical (**1**) is clearly an unusual species. The ring opening of **1** is one of the fastest radical rearrangements known that involves bond breaking. However, our results show that **1** reacts with hydrogen atom donors with rate constants greater than those of simple alkyl radicals, so one must exercise extreme caution in generalizations based on applications of **1** as a radical clock[46] to time a particular radical reaction.[47] Similarly, the highly stereoselective trapping of radical **1** by hydrogen atom donors, which most likely results from a stereoelectronic effect, suggests that conclusions based on trapping experiments must also factor in the properties of the bicyclo[2.1.0]pentyl system. Given these caveats, radical **1** probably should be regarded as a somewhat unique species and a questionable model for other radicals.

Experimental Section

General. Reagents were purchased from Aldrich Chemical Co. *N*-Hydroxypyridine-2-thione was obtained from the corresponding sodium salt (Olin, sodium Omadine) as previously described.[49] THF solvent for kinetic and trapping studies was distilled from sodium benzophenone under nitrogen immediately before use. Thiophenol, 2,6-dimethylthiophenol, and *tert*-butyl mercaptan were distilled from $CaSO_4$.

^{1}H NMR spectra were obtained on a Varian XL 200E FT NMR spectrometer. ^{2}H NMR spectra were obtained on a Varian XL 200 FT NMR spectrometer. Analytical GC was accomplished on Varian 3400 and 2400 gas chromatographs equipped with flame ionization detectors. Wide bore capillary DB-1 and DB-17 columns (J&W Scientific) were used for conventional GC separations. For GC analyses of low-weight hydrocarbon mixtures, a 2.2 m by 3 mm i.d. glass column containing an active phase of $AgNO_3$ in ethylene glycol[50a] on Chromosorb P and a 1.8 m by 6 mm o.d. Teflon column containing an active phase of $AgNO_3$ in diethylene glycol[50b] on Chromosorb P were employed. Preparative GC was accomplished on a Varian 920 chromatograph equipped with thermal conductivity detectors. GC–mass spectral analyses were performed on a Hewlett-Packard (HP) 5790 GC interfaced to an HP 5970 mass selective analyzer; low-polarity columns equivalent to the analytical columns used above were employed.

Benzeneselenol was prepared in 57% yield by reaction of phenylmagnesium bromide with black selenium by the method of Foster.[51] PhSeH was distilled at reduced pressure, and the fraction with bp 55–57 °C (5 Torr) was divided into portions and sealed in glass vials that were stored in the dark and opened under N_2 immediately before use. The purity of PhSeH was checked by GC before use. Samples typically were contaminated with 3–7% of Ph_2Se_2.

Preparation of Deuterated Donors. Thiophenol-*S-d* was prepared from PhSH and D_2O by the method of Lambert and Clikeman;[52] distilled PhSD (bp 70–72 °C, 20 Torr) contained <10% protium on sulfur as determined by ^{1}H NMR spectroscopy. Benzeneselenol-*Se-d* and 2,6-dimethylthiophenol-*S-d* were prepared similarly; the crude products contained <10% protium on selenium (PhSeD) and <5% protium on sulfur (**5-*d***) as determined by ^{1}H NMR spectroscopy and were not further purified.

1-[[(2-Bicyclo[2.1.0]pentyl)carbonyl]oxy]-2(1*H*)pyridinethione (4). Bicyclo[2.1.0]pentane-2-carboxylic acid was prepared by a modification of the method of Brook and Brophy.[53] In the modified method, LDA in THF (rather than NaH in dioxane) was employed in both enolate generation steps. The acid was obtained as a 40:60 exo:endo mixture as determined by ^{1}H NMR spectroscopy. Isomerically pure samples of the *endo*- and *exo*-acid were obtained by conversion of the mixture of acids to the methyl esters (diazomethane in ether), preparative GC (2 m by 6 mm o.d. column, 30% Carbowax 20M on Chromosorb P), and saponification of the esters; analytical GC of the purified methyl ester isomers indicated that they contained <1% of the alternate isomer.

Radical precursor **4** was prepared as a 40:60 exo:endo mixture from the mixture of above acids by reaction of the acids with the salt[9] formed by reaction of *N*-hydroxypyridine-2-thione with phosgene. A solution of the acids (0.50 g, 4.5 mmol) and Et_3N (0.53 g, 5.3 mmol) in 10 mL of CH_2Cl_2 was added dropwise to 1.0 g (5.3 mmol) of the above salt in 20 mL of CH_2Cl_2 in a vessel shielded from light and placed in a 0 °C bath. The reaction was allowed to warm to room temperature, and the mixture was stirred for 6 h. Water (15 mL) was added, and the phases were separated. The organic phase was washed with saturated aqueous NaCl solution (2 × 15 mL) and dried (Na_2SO_4). The solvent was removed under reduced pressure to give a brown oil. The crude oily product was purified by chromatography (silica gel, 1:1 hexanes–ethyl acetate elution) in a column shielded from light. Product **4** was obtained as a yellow-green oil in 51–61% yield in various preparations. The isomer ratio was determined by ^{1}H NMR spectroscopy by integration of the characteristic ^{1}H NMR signals at δ 2.9 (*exo*-**4**) and 3.65 (*endo*-**4**). Isomerically pure samples of *endo*- and *exo*-**4** were prepared by the same procedure from the samples of isomerically pure acids. Samples of PTOC ester **4** decomposed on storage at 0 °C in vessels shielded from light.

For *exo*-**4**, ^{1}H NMR ($CDCl_3$): δ 0.8 (dt, 1 H), 0.95 (ddt, 1 H), 1.8–2.0 (m, 2 H), 2.18 (t, 1 H), 2.7 (ddd, 1 H), 2.9 (t, 1 H), 6.65 (dt, 1 H), 7.2 (m, 1 H), 7.5–7.8 (m, 2 H).

For *endo*-**4**, ^{1}H NMR ($CDCl_3$): δ 0.9 (dt, 1 H), 1.05 (d, 1 H), 1.75 (m, 1 H), 1.9–2.1 (m, 2 H), 2.55 (ddd, 1 H), 3.65 (dt, 1 H), 6.6 (dt, 1 H), 7.2 (m, 1 H), 7.55 (d, 1 H), 7.7 (d, 1 H).

1-[[(Cyclopropylmethyl)carbonyl]oxy]-2(1*H*)-pyridinethione (7) was prepared as previously described.[4]

Product Identification. Authentic bicyclo[2.1.0]pentane was prepared by the method of Gassman and Mansfield.[54] The ^{1}H NMR spectrum agreed with that previously reported.[13] The signal assignments for the *endo*- (δ 1.30) and *exo*-C-2 (δ 2.10) protons were confirmed by decoupling experiments that showed long-range coupling between a signal for a proton on C-5 and the signal assigned to the *exo*-C-2 proton. Analytical GC response factors were determined with authentic samples of

(44) Each donor will react with **1** with two distinct trapping reactions; therefore, the apparent behavior of k_r could be a function of the donor identity.

(45) For example, a tunneling reaction pathway for ring opening would result in a constant value that must be added to k_r.

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(47) For example, the value of k_{OH} for the oxygen rebound step in the cytochrome P-450 oxidation calculated by Ingold et al.[5] might be correct for radical **1** but too large for other radicals. In accord with this prediction, it is interesting to note that in a recent study of P-450 oxidations of methyl-substituted cyclopropanes, Ingold's group[48] determined a value for k_{OH} at 37 °C that was only about half the value derived from the bicyclo[2.1.0]pentane oxidation results.

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cyclopentene and bicyclo[2.1.0]pentane.

Kinetic Studies. The method used was similar to that previously reported.[4] The radical precursor was weighed into a dry, N_2 purged Pyrex tube (20 cm × 10 mm o.d.) equipped with a stirbar, sealed with a septum, and shielded from light with Al foil. The reaction tube was cooled to −78 °C, and the desired amount of trapping agent and nonane (internal standard) in THF was added. Additional THF was added to adjust the solution to a volume of 1 mL. The tube was sealed under vacuum and placed in a thermostated bath; bath temperatures were measured with a thermocouple and are believed to be accurate to within 0.5 °C. After 5 min of equilibration, the shield was removed, and the mixture was irradiated with a 150-W tungsten filament lamp at a distance of about 50 cm for 15–20 min. The tubes were cooled to −78 °C and opened, and the mixture was analyzed by GC. Ratios of low-weight hydrocarbon products were determined on the $AgNO_3$ columns; yields typically were in the range 80–100%, although lower yields were obtained in low-temperature studies with PhSeH trapping (the minimum yield was 56%). GC analyses on the DB-1 column were performed to search for high-weight products; typically, traces (<0.5%) of high-weight products were observed.

In low-temperature reactions with PhSH and PhSeH, bicyclo-[2.1.0]pentane-2-carboxylic acid (mixture of isomers) was detected by GC (DB-1) as a broad peak. For three kinetic runs performed at −78 °C, the reaction mixtures were treated with an excess of freshly prepared diazomethane, and the mixture was analyzed by GC (DB-17) to determine the ratio of *exo*- and *endo*-methyl esters.

Labeling Studies. The reactions were run in a manner similar to the kinetic studies. The reaction tube used was a 10 mm o.d. NMR tube, and the stirbar was omitted. For ArSD studies, the concentration of deuterated thiol was ca. 40 times that of PTOC **4**. For the PhSeD study, a 2-fold excess of donor was employed. The reaction mixtures contained 2–3 mg of benzene-d_6 as an internal reference. Following the reactions, the samples were analyzed by ^2H NMR spectroscopy at 29 MHz; the spectrometer was run in an unlocked mode. ^2H NMR spectra of the deuterated donors in THF showed only very minor signals in the region from δ 0 to 2.5. When referenced to internal benzene-d_6, the signal assignments for the *endo*- and *exo*-bicyclo[2.1.0]pentane-2-*d* were 0.2 ppm upfield of the literature assignments.[55] However, when referenced to external TMS, the signal assignments were *exo*-*d* δ 2.10 (lit.[55] δ 2.11) and *endo*-*d* δ 1.33 (lit.[55] δ 1.33).

For the reaction run at 1.5 °C, the low-weight hydrocarbon products (contaminated with some THF) were isolated as a mixture by preparative GC ($AgNO_3$ in ethylene glycol column). ^2H NMR spectroscopy of this mixture showed the signals for *endo*- and *exo*-bicyclo[2.1.0]pentane-2-*d* and cyclopentene-4-*d* (along with small natural abundance signals from THF) in the same ratio as found in the initial ^2H NMR analysis.

Diffusion Measurements. The method employed was the PGSE experiment described by Stejskal and Tanner[17a] based on the two-pulse spin echo sequence of Hahn[17b] and further adapted to FT techniques by James and McDonald.[17c] Measurements were performed on the Varian XL 200E spectrometer employing the dual 5-mm $^1H/^{13}C$ probe. Sample depths in the 5 mm o.d. NMR tubes were 2.5 cm. Experiments were run in nonspinning, unlocked mode with a recently described PGSE pulse sequence.[17d] ^1H spin echoes were recorded as absolute value spectra. The field gradient generated by the homospoil pulse was calibrated before each run with a sample of absolute MeOH; diffusion coefficients (D) for MeOH were those reported by Sandhu.[18a] A typical value of the field gradient was 150 mG cm^{-1}; the total variation in the field gradient over the course of the studies was about 5%. Values of D obtained for neat samples of cyclohexane, benzene, and chloroform were in good agreement with those previously reported.[18] Reasonable results were obtained over the temperature range −10 to 35 °C; at temperatures outside this range, rapid echo decay was observed presumably due to thermal gradients resulting in bulk convective mixing.

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Homogeneous Catalysis. Catalytic Production of Simple Enols

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Abstract: Complexes of the type $[Rh(diphosphine)(solvent)_2]^+$ in dry acetone or tetrahydrofuran solutions are effective catalysts for generating synthetically useful quantities of simple enols from their corresponding allylic alcohols. A representative collection of simple enols has been produced, and the physical properties and stabilities are recorded. Although these catalysts also ketonize (tautomerize) the enols to their corresponding aldehydes and ketones, the simple enols are conveniently stable in solutions containing the milder catalysts. It is found that in the absence of catalyst simple enols are remarkably stable; the enols of propanal and methyl ethyl ketone persist for up to 2 weeks in dilute acetone solutions at 25 °C. The mechanism of catalysis has been inferred from specific isotopic labeling experiments. The conclusions are as follows: the production of enols involves a hydrogen 1,3-shift mechanism involving hydrido-π-allylic intermediates; the catalytic process is essentially irreversible; and the catalytic ketonization proceeds through a hydrido-π-oxyallylic intermediate. This process is also irreversible, and the stereoselective step is the α-hydrogen abstraction from the allylic substrate. The hydrogen abstraction is probably the turnover limiting step. Three examples of chemical reactions that are unique to enols are reported and are described as proceeding by an ene mechanism.

It was long believed that enols, in the absence of kinetic steric impediments or of thermodynamic electronic stabilization, were fugacious molecules that rapidly tautomerize to the corresponding aldehydes or ketones.[1] Since enols are both acid and base sensitive[2] and possibly are even tautomerized under aprotic conditions by an intermolecular mechanism, devising suitable synthetic conditions for their production has proved elusive. It is probable that the absence of suitably mild synthetic procedures led to the supposition that enols were evanescent entities. Recent work, however, has demonstrated that simple enols can be generated and are sufficiently stable to be studied by conventional techniques. The controlled formation of these species relied on ingenious chemical[3,4] and photochemical[5-7] methods, and the relevant kinetic

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