Clocking Tertiary Cyclopropylcarbinyl Radical Rearrangements[1]

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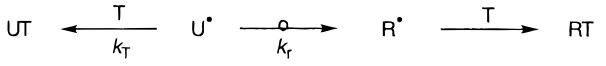
Three independent methods have been employed to estimate the rate constant, k_1, for ring-opening of the 2-cyclopropyl-2-propyl radical, **1**, at room temperature. These three estimates are based on chemical trapping of **1** and the ring-opened 4-methylpent-3-ene-1-yl radical by thiophenol ($k_1 = (1.6_5 \pm 0.4_1) \times 10^7$ M^{-1} s^{-1}), 9-azabicyclo[3.3.1]nonane-N-oxyl ($k_1 = (1.7_6 \pm 0.3_4) \times 10^7$ M^{-1} s^{-1}) and 2,2,6,6-tetramethylpiperidine-*N*-oxyl ($k_1 = (2.1 \pm 0.4) \times 10^7$ M^{-1} s^{-1}) and absolute rate constants for nonrearranging radicals structurally related to **1**. The mean value for k_1 ($(1.8_4 \pm 0.4) \times 10^7$ M^{-1} s^{-1}) should be used when **1** is employed as a tertiary alkyl free radical clock at ambient temperatures.

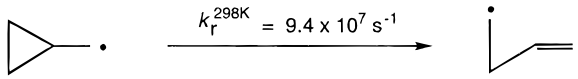
Radicals which undergo unimolecular rearrangements have been described as "free radical clocks".[3] Provided the rate constant, k_r, for conversion of the unrearranged radical, U•, to the rearranged radical, R•, is known (i.e., provided the clock has been calibrated)[3,4] the rate constant, k_T, for any competing reaction involving U• can be calculated by determining the relative yields of the U• and R• derived products, e.g.,



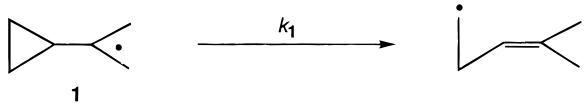
$$k_T = k_r [UT] / [T] [RT] \qquad \text{I}$$

Similarly, if k_T is known for a radical which is structurally similar to U• but which does not undergo rearrangement, then a measurement of the [UT]/[RT] ratio will yield k_r and a new radical clock will have been calibrated.

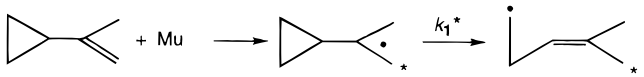
Most cyclopropylcarbinyl radicals rearrange relatively rapidly to give 3-butenyl radicals, e.g.,[3−6]



Cyclopropylcarbinyl radicals make excellent clocks and many, including the parent radical (see above), have been calibrated with high precision.[3−6] However, there is considerable uncertainty regarding the rate of ring-opening of 2-cyclopropyl-2-propyl, **1**, the simplest tertiary cyclopropylcarbinyl radical.



The only "direct" measurement of k_1 involved the addition of muonium (Mu = μ^+e^-), a light isotope of hydrogen, to 2-cyclopropylpropene.[7] The line width of the



muon spin rotation (μSR) spectrum increased with increasing temperature, and from measurements between 233 K and 282 K the following Arrhenius equation for the ring-opening was obtained:

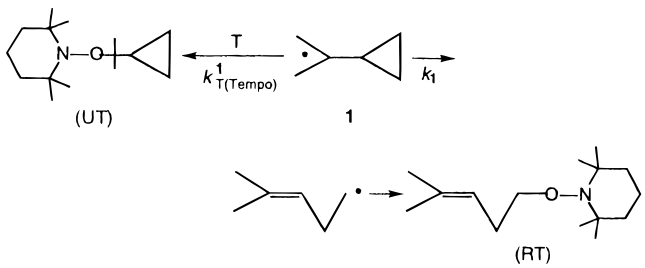
$$\log (k_1^*/\text{s}^{-1}) = 14.5 - 10.4/\theta$$

where $\theta = 2.3RT$ kcal/mol. This equation yields $k_1^{*298\text{ K}} = 7.5 \times 10^6$ s^{-1}, but the Arrhenius parameters are questionable since the preexponential factor should be $10^{13.15}$ s^{-1}.[5,6] If one assumes that values of k_1* measured in the middle of the experimental temperature range are reliable, a revised Arrhenius equation can be calculated:

$$\log (k_1^*/\text{s}^{-1}) = 13.15 - 8.8/\theta$$

which yields $k_1^{*298\text{ K}} = 5.0 \times 10^6$ s^{-1}.

Two "indirect" estimates of k_1 are 1 order of magnitude larger than this direct, μSR-determined rate constant. Both indirect estimates relied on the competitive trapping of **1** with stable nitroxide radicals, Tempo[6] and TMIO,[8] e.g., for T = Tempo:



Analyses for the relative yields of the two hydroxylamine products, UT and RT, and application of eq I yielded rate constant ratios, $k^1_{T(Tempo)}/k_1$.[6] Absolute rate constants for

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(3) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317−323.

(4) For the most recent compilation of calibrated clock reactions, see Newcomb, M. *Tetrahedron* **1993**, *49*, 1151−1176.

(5) Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275−277.

(6) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687−5698.

(7) Burkhard, P.; Roduner, E.; Hochmann, J.; Fischer, H. *J. Phys. Chem.* **1984**, *88*, 773−777.

(8) (a) TMIO is 1,1,3,3-tetramethylisoindoline-2-oxyl. (b) Beckwith, A. L. J.; Bowry, V. W. *J. Am. Chem. Soc.* **1994**, *116*, 2710−2716.

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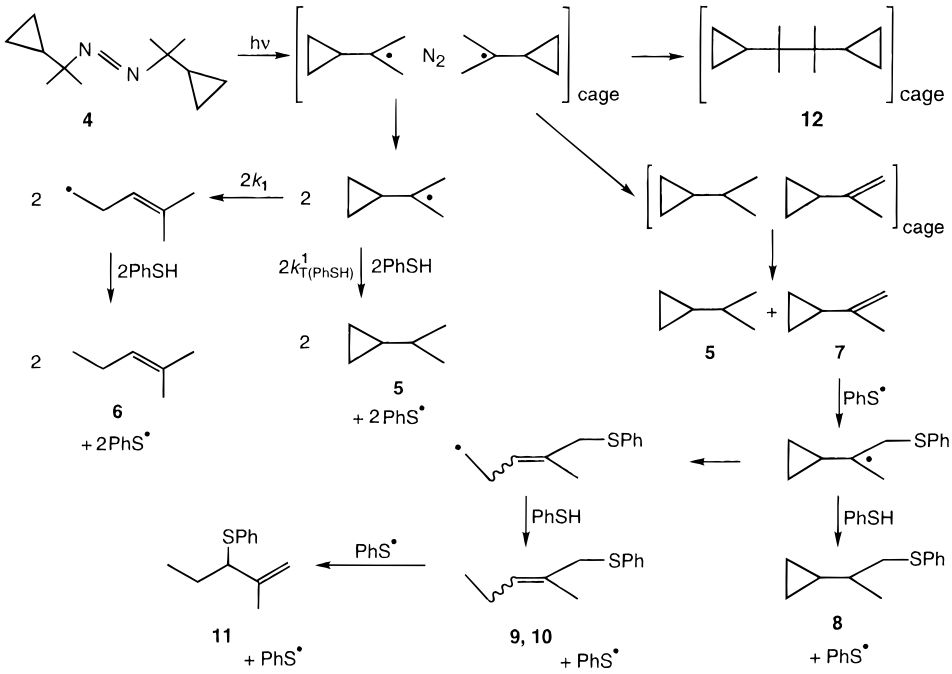
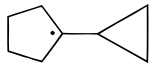
Scheme 1



the trapping of a variety of carbon-centered radicals by nitroxides have been measured by laser flash photolysis (LFP).[6,9−11] These reactions are somewhat slower than diffusion-controlled and are subject to considerable solvent[10] and steric[11] effects. In the Tempo/**1** trapping experiment[6] it was assumed that the *tert*-butyl radical was a suitable model for **1**, i.e., it was *assumed* that $k^{\mathbf{1}}_{\mathrm{T(Tempo)}}$ was equal to the LFP measured rate constant for *tert*-butyl trapping by Tempo, $k^{\mathrm{Me_3C}}_{\mathrm{T(Tempo)}}$. With this assumption $k_{\mathbf{1}}^{298\ \mathrm{K}}$ was estimated to be $5.3 \times 10^7\ \mathrm{s}^{-1}$.[6] A somewhat analogous series of assumptions using TMIO as the trap gave $k_{\mathbf{1}}^{298\ \mathrm{K}} = 4.2 \times 10^7\ \mathrm{s}^{-1}$.[8b]

The ring openings of the two bicyclic radicals, **2** and **3,** have also been studied using thiophenol to trap the unrearranged and rearranged radicals.[12] With the assumption that Franz et al.'s[13] LFP measured rate constant for the *tert*-butyl/thiophenol reaction, $k^{\mathrm{Me_3C}}_{\mathrm{T(PhSH)}}$, is equal to $k^{\mathbf{1}}_{\mathrm{T(PhSH)}}$ values of $k_{\mathbf{2}}^{298\ \mathrm{K}}$ and $k_{\mathbf{3}}^{298\ \mathrm{K}}$ were calculated to be $1.5 \times 10^7\ \mathrm{s}^{-1}$ and $1.1 \times 10^7\ \mathrm{s}^{-1}$, respectively.[12]



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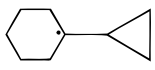


3

One order of magnitude disagreement regarding the correct value of $k_{\mathbf{1}}$ is unacceptable if **1** is to be useful as a calibrated radical clock. A more reliable value for $k_{\mathbf{1}}$ would permit the calculation of more reliable triplet lifetimes for several biradicals[14] and the calculation of other kinetic parameters.[15] We present, herein, our attempts to refine $k_{\mathbf{1}}$.

Results

To obtain $k_{\mathbf{1}}$ we have employed three procedures: (i) trapping **1** with thiophenol, (ii) trapping **1** with 9-azabicyclo[3.3.1]nonane-*N*-oxyl (ABNO), (iii) measurement by LFP of the rate constant for trapping by Tempo of the 2,3-dimethylbut-2-yl radical (chosen because it would appear to be a much better model for **1** than the *tert*-butyl radical whenever steric effects might be important).

(i) Thiophenol Trapping. The azo compound, **4**,[16] was photolyzed in fluorobenzene at 22 °C in the presence of known concentrations of thiophenol (as described in earlier work with **2** and **3**).[12] The chemistry (Scheme 1) was found to be complicated both by the formation of some isopropylcyclopropane, **5**, by the in-cage disproportionation of photogenerated **1** pairs and by various addition reactions involving the phenylthiyl radical and the alkenes formed in the overall reaction. A kinetic analysis of Scheme 1 yields the following relationship:[17]

$$\frac{k^{\mathbf{1}}_{\mathrm{T(PhSH)}}}{k_{\mathbf{1}}} = \frac{1}{[\mathrm{PhSH}]_{\mathrm{avg}}} \times \frac{\mathbf{5} - (\mathbf{7} + \mathbf{8} + \mathbf{9} + \mathbf{10} + \mathbf{11})}{\mathbf{6}}$$

where the structure numbers refer to the measured yields of the indicated compounds (see Table 1). The conversion of the azo compound, **4**, was about 40%, and product

(9) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 1629−1632.

(10) Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983−4992.

(11) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4992−4996.

(12) Engel, P. S.; Culotta, A. M. *J. Am. Chem. Soc.* **1991**, *113*, 2686−2696.

(13) Franz, J. A.; Bushaw, B. A.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 268−275.

(14) See e.g., Engel, P. S.; Keys, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 6860−6861. Engel, P. S.; Keys, D. E.; Kitamura, A. *J. Am. Chem. Soc.* **1985**, *107*, 4964−4975. Adam, W.; Grabowski, S.; Scherhag, F. *Tetrahedron Lett.* **1988**, *29*, 5637−5640. Engel, P. S.; Lowe, K. L. *Tetrahedron Lett.* **1994**, *35*, 2267−2270.

(15) See e.g., Engel, P. S.; Wu, A.-Y. *J. Org. Chem.* **1994**, *59*, 3969−3974.

(16) Timberlake, J. W.; Martin, J. C. *J. Org. Chem.* **1968**, *33*, 4054−4060.

(17) The in-cage disproportionation/combination ratio for **1** pairs, which is given by the product ratio, (**7** + **8** + **9** + **10** + **11**)/[**12**], is 6.3 ± 0.3. This value is similar to the disproportionation/combination ratio for pairs of *tert*-butyl radicals at ambient temperatures in solvents of similar viscosity to fluorobenzene.[18] The cage effect calculated from the amount of **4** which reacted and from the product ratio, (**7** + **8** + **9** + **10** + **11** + **12**)/{[**12**] + (**5** + **6** + **7** + **8** + **9** + **10** + **11**)/**2**} were in good agreement, viz., 0.54 ± 0.03 and 0.59 ± 0.03, respectively.

Table 1. Product Yields and Derived Kinetic Quantities from the Photolysis of 4 in C_6H_5F at 22 °C in the Presence of PhSH[a]

$[PhSH]_o$[b]	0.039	0.059	0.098	0.147	0.196	0.294
$[PhSH]_{avg}$[c]	0.028	0.049	0.089	0.142	0.194	0.292
% **4** left[d]	41.2	42.2	41.3	39.2	41.1	38.9
prod. bal %[e]	87.7	87.6	94.4	82.0	89.4	91.0
5[f]	3.17	3.64	4.36	4.43	4.86	5.48
6[f]	3.01	2.61	2.21	1.60	1.38	1.08
7[f]	0.66	0.13	nd[g]	nd[g]	nd[g]	nd[g]
8[f]	nd[g]	0.14	0.27	0.34	0.49	0.71
9[f]	0.45	0.53	0.63	0.50	0.54	0.52
10[f]	1.09	1.25	1.48	1.20	1.26	1.22
11[f]	0.14	0.17	0.20	0.15	0.16	0.16
12[f]	0.37	0.38	0.40	0.36	0.38	0.39
trap/rear[h]	0.275	0.539	0.799	1.393	1.731	2.636
disp/comb.[i]	6.36	5.84	6.47	6.07	6.55	6.67
cage[j]	0.53	0.52	0.59	0.49	0.46	0.57
cage[k]	0.59	0.56	0.60	0.57	0.60	0.60

[a] Initial **4** is 8.64 μmol in 0.5 mL of C_6H_5F. [b] Initial PhSH concentration, M. [c] Average PhSH concentration, M, during the run based on GC. [d] Remaining **4** at the end of the run, by GC. [e] Product balance. [f] Product yield, μmol. For structures, see Scheme 1. [g] Not detected. [h] Trapped **1**/rearranged **1** = {**5** − (**7** + **8** + **9** + **10** + **11**)}/**6**. [i] In cage disproportionation/combination ratio = (**7** + **8** + **9** + **10** + **11**)/(**12**), see footnote 17. [j] Total yield of cage products (Σ **7** → **12**) divided by the amount of **4** which was photolyzed, see footnote 17. [k] Cage effect calculated from the product ratio: (Σ **7** → **12**)/{**12** + Σ (**5** → **11**)/2}; see footnote 17.

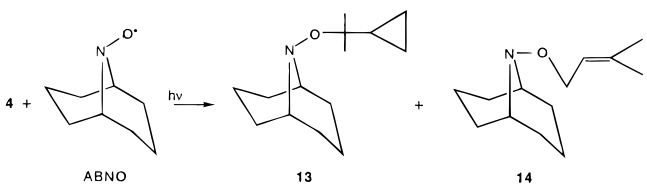
Table 2. Product Ratios from the Photolysis of 4 in C_6H_5F at 22 °C in the Presence of ABNO

$[ABNO]_{init}$ (M)	$[ABNO]_{avg}$ (M)	**13**/**14**
6.0×10^{-3}	3.0×10^{-3}	0.11_2
8.0×10^{-3}	4.0×10^{-3}	0.15_8
1.2×10^{-2}	7.0×10^{-3}	0.28_4
1.6×10^{-2}	$1.1_6 \times 10^{-2}$	0.42_7
2.0×10^{-2}	1.6×10^{-2}	0.56_7
2.5×10^{-2}	$2.1_6 \times 10^{-2}$	0.73_0

balances ranged from 82 to 91%. Despite the fact that PhSH conversions were as high as 58%, the plot of {**5** − (**7** + **8** + **9** + **10** + **11**)}/**6** vs the average PhSH concentration in each experiment, $[PhSH]_{avg}$, was linear with a correlation coefficient of 0.998. The slope of this plot yields $k^{\mathbf{1}}_{T(PhSH)}/k_{\mathbf{1}} = 8.46 \pm 0.29\ M^{-1}$ at 22 °C.

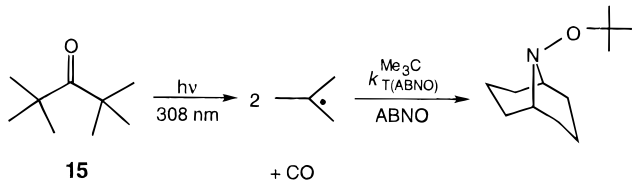
(ii) ABNO Trapping. The Bredt's rule-protected bicyclic nitroxide, ABNO, is known to be an excellent trap for alkyl radicals.[10,11] Of more importance in the present context, the rate constants for alkyl radical trapping by ABNO are much less sensitive to the steric demands of the alkyl radical than is the case for Tempo and TMIO.[11] This means that the *tert*-butyl radical will be a better model for **1** in ABNO trapping than it will be in Tempo trapping experiments.

Photolysis of ca. 50% of the azo compound, **4**, (0.02M initial) in fluorobenzene at 22 °C in the presence of ABNO gave the two expected hydroxylamines, **13** and **14**. The **13**/**14** ratios at various ABNO concentrations are given in Table 2. A plot of the **13**/**14** ratio vs average ABNO



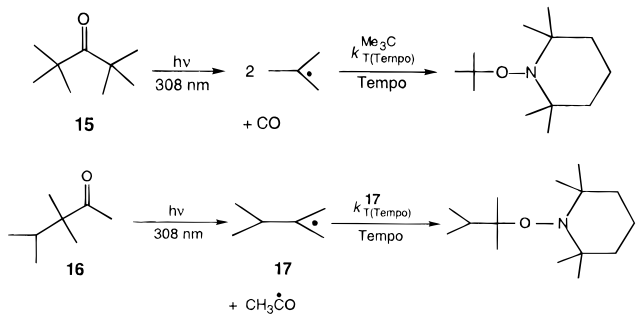
concentration gave a straight line with a correlation coefficient of 0.998 and a slope equal to $k^{\mathbf{1}}_{T(ABNO)}/k_{\mathbf{1}} = 32.4 \pm 1.1\ M^{-1}$.

The rate constant for trapping of the *tert*-butyl radical by ABNO was measured at 20 °C by 308 nm LFP. The solvent was again fluorobenzene so as to eliminate any solvent effects on this rate constant. The *tert*-butyl radicals were generated from di-*tert*-butyl ketone, **15**, and their decay was monitored directly at 320 nm via their weak absorption at this wavelength.[19] The experimental pseudo-first-order rate constants for *tert*-butyl decay,



k_{exptl}, were measured at various ABNO concentrations. A plot of k_{exptl} vs [ABNO], i.e., $k_{exptl} = k_o + k^{Me_3C}_{T(ABNO)}$ [ABNO], gave a straight line the slope of which yielded $k^{Me_3C}_{T(ABNO)} = (5.7 \pm 0.9) \times 10^8\ M^{-1}\ s^{-1}$.

(iii) Tempo Trapping of the 2,3-Dimethylbut-2-yl Radical. The *tert*-butyl radical and 2,3-dimethylbut-2-yl radical, **17**, were generated by 308 nm LFP of ketones **15** and **16**, respectively, in benzene[20] at 20 °C in the presence of various known concentrations of Tempo. The



decays of these two tertiary carbon-centered radicals were monitored directly via their weak absorptions at 320 nm. The advantage of directly monitoring the kinetics of decay of **17** is that any reactions of the simultaneously produced acetyl radical are "invisible". Plots of k_{exptl} vs [Tempo] yielded $k^{Me_3C}_{T(Tempo)} = (2.5 \pm 0.4) \times 10^8\ M^{-1}\ s^{-1}$ and $k^{\mathbf{17}}_{T(Tempo)} = (1.0 \pm 0.2) \times 10^8\ M^{-1}\ s^{-1}$. Thus, **17** reacts ca. 2.5 times more slowly with Tempo than the *tert*-butyl radical.

Discussion

Our work allows three different estimates to be made of the rate constant, $k_{\mathbf{1}}$, for the ring-opening of the cyclopropyldimethylcarbinyl radical, **1**, at ambient temperatures. These three estimates are based on "indirect" measurements since they all rely on the chemical trapping of **1** (by PhSH, ABNO, and Tempo) and assumptions about which nonrearranging radical is an appropriate model for estimating the absolute rate constants for the

(18) See, e.g., Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, *73*, 441−464. Shuh, H.; Fischer, H. *Int. J. Chem. Kin.* **1976**, *8*, 341−356. Shuh, H. H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2463−2481. Tanner, D. D.; Rahimi, P. M. *J. Am. Chem. Soc.* **1982**, *104*, 225−229.

(19) See, e.g., Huggenberger, C.; Fischer, H. *Helv. Chim. Acta* **1981**, *64*, 338−353. Chatgilialoglu, C.; Ingold, K. U.; Lusztyk, J.; Nazran, A. S. Scaiano, J. C. *Organometallics* **1983**, *2*, 1232−1235.

(20) The absorption of **16** was blue-shifted in C_6H_5F relative to C_6H_6 and, with only a very limited supply of **16**, it proved impossible to do the LFP experiments in C_6H_5F.

trapping of **1**. These three estimates of k_1 are in remarkably close agreement.

(i) Steric effects on the rates of hydrogen atom abstraction from thiophenol by carbon-centered radicals would appear to be small.[13] It is therefore reasonably safe to assume that **1** can be modeled by the *tert*-butyl radical for which the thiophenol trapping rate constant has been measured by LFP.[13] From the reported Arrhenius parameters[13] we calculate that $k^{Me_3C}_{T(PhSH)} = (1.4 \pm 0.3) \times 10^8$ M^{-1} s^{-1} at 22 °C. If this rate constant is combined with the result of our thiophenol trapping experiment, viz., $k^{1}_{T(PhSH)}/k_1 = 8.46 \pm 0.29$ M^{-1}, we obtain $k_1 = (1.6_5 \pm 0.4_1) \times 10^7$ s^{-1}.

(ii) Steric effects on the rates of carbon-centered radical additions to ABNO are also small[11] and so we will again assume that the *tert*-butyl radical is a suitable model for **1**. Combining our LFP measured rate constant, $k^{Me_3C}_{T(ABNO)} = (5.7 \pm 0.9) \times 10^8$ M^{-1} s^{-1} with the result of our ABNO trapping experiments, viz., $k^{1}_{T(ABNO)}/k_1 = 32.4 \pm 1.1$ M^{-1} yields $k_1 = (1.7_6 \pm 0.3_4) \times 10^7$ s^{-1}.

(iii) The trapping by Tempo of carbon-centered radicals is known to be rather strongly influenced by the steric requirements of the carbon radical.[11] The 2.5 fold slower Tempo trapping of the 2,3-dimethylbut-2-yl radical, **17**, relative to the *tert*-butyl radical is, therefore, not too surprising. If we assume that **17** is an appropriate model for **1**, our original estimate[6] that k_1 was equal to 5.3×10^7 s^{-1} (with a probable error of ± 20%) should be reduced by a factor of 2.5. This yields a corrected $k_1 = (2.1 \pm 0.4) \times 10^7$ s^{-1}.[21]

Thus, our three separate estimates of the rate constant for the ring-opening of the cyclopropyldimethylcarbinyl radical, **1**, are in rather satisfactory agreement. We therefore believe that their mean value at ambient temperatures, viz., $k_1 = (1.8_4 \pm 0.4) \times 10^7$ s^{-1} should be fairly reliable.[22] We are at a loss to explain why our present estimate of k_1 is three times (or more probably four times, see Introduction) larger than would be implied on the basis of the "direct" μSR measurements.

Experimental Section

Instrumentation. NMR spectroscopy: IBM AF-300 or Bruker AC-250 with δ relative to either $CDCl_3$ (δ 7.26) or C_6D_6 (δ 7.15). IR spectroscopy: Nicolet 205 FT-IR. Mass spectrometry: Finnigan MAT 95, all HRMS were obtained in CI mode. UV spectroscopy: HP8452A diode array spectrometer. Analytical GC: HP5890A with a DB-5 capillary column (0.25 mm × 30 m) and HP3365 software. Preparative GC: Antek 300 with a 0.25 in × 10 ft 10% FFAP on Chromosorb W column.

Materials. Ether and THF were distilled from Na/Ph_2CO, hexane was distilled from sodium, and benzene and CH_2Cl_2 were distilled from CaH_2. Decane, used as a GC internal standard, was distilled. Thiophenol was distilled immediately before use. Tempo was sublimed, and di-*tert*-butyl ketone was passed through basic alumina prior to use. 2-Cyclopropylpropane, 2-methyl-2-pentene, and (*E*)-2-methyl-2-pentenoic acid (all from Aldrich) were used as received.

2,2′-Dicyclopropyl-2,2′-azopropane, 4, first synthesized by Timberlake and Martin[16] was prepared in much improved yield using the method developed by Duismann *et al*.[23] for bis-*tert*-alkyl azo compounds. To cyclopropylmethyl ketone (2.4 mL, 25 mmol) in 10 mL of hexane at room temperature was added hydrazine hydrate (0.7 mL, 14 mmol), and the mixture was refluxed for 20 h. Additional hexane (20 mL) was added, and the solution was washed with water and brine. The organic layer was dried over K_2CO_3, filtered, and concentrated to give 1.6 g of cyclopropylmethyl ketone azine (84%). ^{1}H-NMR (250 MHz, $CDCl_3$): 0.88 (m, 4H), 1.01 (m, 4H), 1.93 (m, 2H), 2.23 (s, 6H). Gaseous Cl_2 was bubbled through a solution of this azine (1.0 g, 6.1 mmol) in 25 mL of hexane at −60 °C until a yellow color appeared. The 2,2′-dicyclopropyl-2,2′-dichloro-2,2'-azoethane precipitated as a white solid, and the excess Cl_2 was removed rapidly under aspirator vacuum. After evaporation of the hexane, the residue was recrystallized from hexane at −30 °C, yielding 0.85 g (52%) of product. ^{1}H-NMR (250 MHz, $CDCl_3$) 0.54−0.67 (m, 8H), 1.55 (m, 2H), 1.81 (s, 6H); MS (70 eV), *m*/*e* (%) 234 (1), 199 (18), 103 (100), 67 (80), 41 (50); UV (hexane) λ_{max} 366 nm, ϵ = 22. This α,α′-dichloroazoalkane was converted to **4** as follows. A 1 mL portion of 2 M Me_3Al in hexane was diluted with 5 mL of hexane and cooled to −70 °C. A solution of α,α′-dichloroazoalkane (120 mg, 0.5 mmol) in 1 mL of hexane was added under Ar. The reaction mixture was stirred for 30 min at −70 °C and was then allowed to warm to room temperature and was stirred for a further 2.5 h, after which time it was recooled to −10 °C and quenched by carefully adding a mixture of hexane/ethanol (4:1) and aqueous H_2SO_4 (10%). Additional hexane (60 mL) was added and the organic layer was separated. After drying over $MgSO_4$ and filtering, evaporation of the solvent gave crude **4**. Further purification of **4** was carried out by column chromatography (EtOAc/hexane 0.05:1); yield 81 mg (81%). Liquid, ^{1}H-NMR (250 MHz, C_6D_6) 0.31 (m, 4H), 0.41 (m, 4H), 1.00 (m, 2H), 1.11 (s, 12H); in reasonable agreement with the literature;[16] ^{13}C-NMR (62.5 MHz, $CDCl_3$) 0.29, 20.57, 24.11, 66.88; MS (70 ev), *m*/*e* (%) 153 (1%), 83 (100), 55 (95), 41 (28); IR (neat) 2973 (s), 1463 (m), 1358 (m), 1168 (m, br) cm^{-1}; UV (hexane) λ_{max} 366 nm, ϵ = 16.5 (lit.[16] λ_{max} 372 nm, ϵ = 22).

2-Cyclopropylpropene, 7, was prepared in 98% yield from cyclopropyl methyl ketone according to a literature procedure.[24] Liquid, ^{1}H-NMR (250 MHz, $CDCl_3$) 0.35 (m, 2H), 0.55 (m, 2H), 1.29 (m, 1H), 1.53 (s, 3H), 4.55 (d, 1H, J = 0.2 Hz), 4.62 (d, 1H, J = 0.2 Hz) in good agreement with the literature.[24]

2-Cyclopropyl-1-(phenylthio)propane,[25] **8**. A solution of PhSSPh (79 mg, 0.36 mmol) in 3 mL of PhSH in a Pyrex tube was purged with nitrogen for 20 min, after which 2-cyclopropylpropene (60 mg, 0.73 mmol) was added and the tube was irradiated (313 nm) for 2.5 h. The mixture was diluted with hexane (30 mL) and washed twice with aqueous NaOH (5%), twice with water, and with brine. The organic layer was dried over $MgSO_4$. Evaporation of solvents and column chromatography (hexane) gave, according to GC, a mixture of four compounds (120 mg, 86%). The retention time of the smallest peak (0.5%) coincided with that of **11** while the other two peaks (4.6% and 1.9%) coincided with **9** and **10** (see below). The **9**:**10** ratio found in this preparation (2.42) was the same as was found in the photolysis of **4** in the presence of PhSH. The major product **8**, which constituted 93% of the mixture, was isolated by preparative TLC (91 mg), and its NMR spectrum showed the AMX pattern expected for the $PhSCH_2CH$ group. Liquid, ^{1}H-NMR (300 MHz, $CDCl_3$) 0.09 (m, 2H), 0.46 (m, 2H), 0.62 (m, 1H), 0.99 (m, 1H), 1.10 (d, 3H, J = 6.4 Hz), 2.83 (dd, 1H, J_1 = 8.1 Hz, J_2 = 12.5 Hz), 3.17 (dd, 1H, J_1 = 4.8 Hz, J_2 = 12.5 Hz), 7.14−7.33 (m, 5H), in satisfactory agreement with the literature[25] provided 1.82 in this reference is a misprint

(21) Since the absolute rate constants for trapping of a wide variety of carbon-centered radicals by Tempo and by TMIO[8a] under the same experimental conditions are very similar,[11] it would appear reasonable to use the same factor of 2.5 to correct the TMIO-derived value of k_1 equal to 4.2×10^7 s^{-1},[8b] which yields a corrected $k_1 = 1.6_8 \times 10^7$ s^{-1}.

(22) For comparison, the 25 °C rate constant for ring-opening of the primary cyclopropylmethyl radical is well established as 9.4×10^7 s^{-1},[4,5] and for the ring-opening of the secondary 1-cyclopropylethyl radical the reported Arrhenius parameters yield 25 °C rate constants of 1.3×10^7 s^{-1},[7] 2.9×10^7 s^{-1},[8b] and 4.5×10^7 s^{-1}.[6]

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for 2.82; ^{13}C-NMR (62.5 MHz, $CDCl_3$) 3.50, 4.44, 17.54, 19.13, 38.64, 40.95, 125.39, 128.51, 128.72, 137.58; HRMS, Cald. for $C_{12}H_{16}S$: 192.09727. Found: 192.09721.

2-Methyl-1-(phenylthio)pent-2-ene, 9 and 10. (*E*)-2-Methyl-2-pentenol[26] was prepared by $LiAlH_4$ reduction of (*E*)-2-methyl-2-pentenoic acid. ^{1}H-NMR (250 MHz, $CDCl_3$) 0.96 (t, 3H, J = 7.5 Hz), 1.66 (s, 3H), 2.10 (m, 2H), 3.99 (s, 2H), 5.4 (t, 1H, J = 6.5 Hz). This alcohol was converted to **9** and **10** as follows: (*E*)-2-methyl-2-pentenol (600 mg, 6 mmol) in 9 mL of ether and 4 mL of HMPA was treated at room temperature with 4.6 mL of 1.3 M MeLi in ether, followed by TsCl (1.2 g, 6.1 mmol) in 5 mL of ether and 2 mL of HMPA. A solution of PhSLi (1.32 g, 12 mmol) in 5 mL of ether and 2 mL of HMPA was added, and the reactants were stirred overnight. A white solid precipitated. Ether (50 mL) was added, the mixture was washed with water four times, and the organic layer was dried over $MgSO_4$. After filtration and evaporation of solvents, the mixture of *E*,*Z* products was isolated by column chromatography (hexane). The yield was 820 mg (72%, *E*:*Z* = 6:1). Liquid, HRMS, Calcd for $C_{12}H_{16}S$: 192.09727. Found: 192.09752. Although the *E*,*Z* mixture was never separated, the individual NMR spectra could be deduced by inspection: **9**, ^{1}H-NMR (250 MHz, $CDCl_3$) 0.86 (t, 3H, J = 7.5 Hz), 1.74 (s, 3H), 2.00 (m, 2H), 3.49 (s, 3H), 5.20 (m, 1H), 7.25−7.45 (m, 5H); ^{13}C-NMR (62.5 MHz, $CDCl_3$) 13.88, 15.01, 21.31, 44.32, 126.2, 127.5, 128.6, 130.5, 131.4, 136.5; **10**, ^{1}H-NMR (250 MHz, $CDCl_3$) 0.84 (t, 3H, J = 7.5 Hz), 1.87 (s, 3H), 1.95 (m, 2H), 3.55 (s, 3H), 5.29 (m, 1H), 7.15−7.45 (m, 5H); ^{13}C-NMR (62.5 MHz, $CDCl_3$) 14.23, 22.37, 29.70, 36.36, 126.4, 128.7, 129.5, 130.6, 136.8, 137.2.

2-Methyl-3-(phenylthio)-1-pentene, 11, was prepared from 3-chloro-2-methylpropene following a literature procedure.[27] To a suspension of sodium methoxide (1.8 g, 30 mmol) in methanol (40 mL) was added PhSH (3.3 g, 30 mmol) at room temperature. After 30 min, 3-chloro-2-methylpropene (3.6 g, 40 mmol) was added, and the reaction mixture was stirred for 3 h. Following removal of a white precipitate, the filtrate was diluted with ether (100 mL) and washed 3× with water. After drying over $MgSO_4$ and filtering, the solvent was rotary evaporated, and the residue was distilled under vacuum to yield 4.2 g of phenyl methallyl sulfide (82%, 78−80 °C/1.8 mmHg). ^{1}H-NMR (250 MHz, $CDCl_3$) 1.87 (s, 3H), 3.54 (s, 2H), 4.83 (s, 2H), 7.21−7.38 (m, 5H). BuLi (1.6 mL, 2.5 M in hexane) was added at −78 °C to this sulfide (656 mg, 4 mmol) dissolved in THF (10 mL), causing a yellow coloration. After 20 min EtI (858 mg, 5.5 mmol) was added and the yellow color disappeared. The reaction mixture was warmed to room temperature for 2 h. Water (10 mL) was added, and the solution was extracted with ether (3 × 50 mL). The ether solution was dried over $MgSO_4$, filtered and concentrated. Flash chromatography gave pure **11** (690 mg, 91%). Oil, ^{1}H-NMR (250 MHz, $CDCl_3$) 0.98 (t, 3H, J = 7.3 Hz), 1.73 (m, 2H), 1.77 (s, 1H) 3.55 (m, 1H), 4.64 (s, 1H), 4.75 (m, 1H), 7.23−7.39 (m, 5H); ^{13}C-NMR (62.5 MHz, $CDCl_3$) 12.17, 17.61, 25.78, 58.09, 113.6, 126.8, 128.5, 132.4, 135.5, 143.5; IR (neat) 2966 (s), 1480 (s), 1438 (s), 1087 (m), 894 (s) cm^{-1}; HRMS, Calcd for $C_{12}H_{16}S$: 192.09727. Found: 197.09709.

Isolation of 2,3-Dicyclopropyl-2,3-dimethylbutane, 12. A 39 mg portion of **4** in a Pyrex tube was irradiated (366 nm) under nitrogen for 2 h after which 0.5 mL of hexane was added, and **12** was isolated by preparative GC (9 mg, 25%). Liquid, ^{1}H-NMR (250 MHz, $CDCl_3$) 0.15−0.30 (m, 8H), 0.71 (s, 12H), 0.98 (m, 2H); ^{13}C-NMR (62.5 MHz, $CDCl_3$) 0.93, 17.51, 20.43, 37.87; HRMS, Calcd for $C_{12}H_{22} + H^+$: 167.17998. Found: 167.18043.

9-Azabicyclo[3.3.1]nonane-*N*-oxyl, ABNO, was synthesized by the method employed previously[10,28,29] except that phenylselenol was used to demethylate *N*-methyl-9-azabicyclo-[3.3.1]nonane.[30]

3,3,4-Trimethyl-2-pentanone,[31−33] **16,** was prepared by methylation of isovaleronitrile with lithium isopropylcyclohexylamide and CH_3I followed by treatment with CH_3Li. The overall yield was 65%. Liquid, ^{1}H-NMR (250 MHz, $CDCl_3$) 0.83 (d, 6H, J = 7.0 Hz), 1.01(s, 6H), 2.00 (m, 1H), 2.13 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) 17.33, 20.20, 24.99, 33.63, 50.79; IR (neat) 1700 cm^{-1}.

Photolyses. Unless otherwise noted, all samples for photolysis were degassed and sealed in 5-mm standard wall Pyrex tubes. Irradiations were carried out with a 500-W Oriel high-pressure mercury lamp employing either a 313 nm or a 366 nm filter solution. The tubes were cracked open and the contents analyzed by GC using the following conditions: injector, 200 °C; detector, 250 °C; oven, 35 °C for 2.5 min and then ramp at 10 °C/min. The weight response factor of **8** relative to decane was established as 0.647, and all of the other sulfides were assumed to have the same response factor. Authentic samples of 2-methyl-2-(phenylthio)pentane, 2-methyl-3-(phenylthio)pentane, 2-cyclopropyl-2-(phenylthio)propane, and 4-methyl-1-(phenylthio)-3-pentene were prepared and found to be absent from the products formed by the irradiation of **4** with thiophenol. ABNO was shown to be photostable by irradiating it in fluorobenzene for 60 min, twice the time of the azoalkane runs. This control experiment showed no decrease in the visible absorbance, consistent with the literature on photolysis of nitroxyl radicals.[34,35] To check the stability of the hydroxylamines to GC, a sample of **4** was irradiated with ABNO in C_6D_6 in an NMR tube until **4** was gone. The ratio of **13** to **14** found by GC was the same as that determined by NMR. This observation and the symmetrical shape of their GC peaks showed the stability of these hydroxylamines to GC analysis; in fact, we were also able to quantify **4** and ABNO itself in the same run.

Laser Flash Photolysis (LFP). The equipment and experimental procedures have been described previously.[36] The *tert*-butyl radical and 2,3-dimethylbut-2-yl radical, **17**, were generated by 308 nm LFP of solutions containing their ketone precursors (di-*tert*-butyl ketone and 3,3,4-trimethyl-2-pentanone, respectively) at a concentration giving an optical density of ∼0.3 at 308 nm. The decays of these tertiary alkyl radicals were directly monitored at 320 nm.[19] Pseudo-first-order rate constants (k_{exptl}) were determined by fitting digitally averaged decay curves from 10 laser flashes. Absolute second-order rate constants were calculated by least-squares fitting of k_{exptl} vs [TEMPO] (or [ABNO]) for five different nitroxide concentrations in the range (0.6−5.0) × 10^{-3} M.

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