

Kinetics and Equilibrium Constants for Reactions of α -Phenyl-Substituted Cyclopropylcarbinyl Radicals

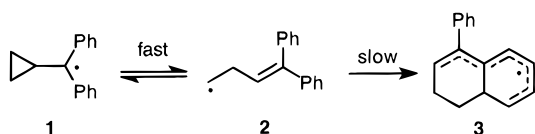
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Abstract: Laser-flash photolysis methods were used to determine Arrhenius functions for cyclizations of the 4,4-diphenyl-3-butenyl (**2**) and *trans*-4-phenyl-3-butenyl (**5**) radicals to the 1,1-diphenylcyclopropylcarbinyl (**1**) and 1-phenylcyclopropylcarbinyl (**4**) radicals, respectively. At 20 °C, the cyclization rate constants are 1.7×10^7 and 5.4×10^6 s⁻¹. Equilibrium constants for the two processes were estimated and evaluated with thermochemical data and via computational methods, and Arrhenius functions for the ring-opening reactions of the cyclopropylcarbinyl radicals were calculated. The cyclization reactions of **2** and **5** are strongly enthalpy controlled. Production of radicals **1** and **2** from the corresponding *tert*-butylperoxy esters in the presence of Et₃SnH gave diphenylcyclopropylmethane and 1,1-diphenyl-1-butene from H-atom trapping of radicals **1** and **2** and 4-phenyl-1,2-dihydronaphthalene which derives from the product radical formed by addition of the radical moiety in **2** to the *cis*-phenyl group. Rate constants for the latter cyclization of **2** and for reactions of radicals **1** and **2** with Et₃SnH were obtained from the indirect kinetic studies.

The 1,1-diphenylcyclopropylcarbinyl radical (**1**) and its acyclic isomer, the 4,4-diphenyl-3-butenyl radical (**2**), were the subjects of a report by Halgren et al. three decades ago.² The objectives of the work were to determine whether **1** and **2** were discrete species or resonance forms of a nonclassical radical and, if discrete species, to evaluate the relative stabilities and reactivities of **1** and **2**. The first point was resolved in favor of discrete species by analyses of product distributions from reactions of the radicals with hydrogen-atom transfer agents. Kinetic models involving rapid equilibration of **1** and **2** with relatively slow and irreversible cyclization of radical **2** to radical **3** were consistent with the product ratios, but the model of reactions from a nonclassical radical required implausible kinetic and thermodynamic values.³ The second objective was accomplished by deriving Arrhenius parameters for absolute and relative kinetic quantities of interest from a detailed mechanistic analysis,³ but the absolute rate constants and the equilibrium constant for equilibration of **1** and **2** were rendered uncertain by the need to apply thermochemical assumptions that could not be independently validated.



Cyclopropylcarbinyl radicals have been the focus of numerous studies in the intervening years, some of which have had

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(2) Halgren, T. A.; Howden, M. E. H.; Medof, M. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 3051–3052.

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objectives similar to those originally presented for **1**. In a report focusing on the utility of “benzylic” cyclopropylcarbinyl radicals as radical clocks in mechanistic studies, Bowry et al. showed that the equilibrium between **4** and **5** favors the cyclic benzylic radical **4** and determined a rate constant for cyclization of **5** at 42 °C by an isotopic scrambling approach.⁴ More recently, Beckwith and Bowry determined Arrhenius parameters for ring opening of **4** and cyclization of **5** by competition kinetics employing nitroxyl radical trapping.⁵ The extent of resonance stabilization of a radical by a cyclopropyl group was addressed experimentally by Walton via low-temperature ESR studies of methylene rotation in the cyclopropylcarbinyl radical.⁶ In addition, high-level calculations of the cyclopropylcarbinyl radical, made possible by the small number of atoms and the rigidity of the ring, have been carried out.^{7,8}



Despite recent related work, the equilibrium between radicals **1** and **2** and the rates of the reactions have not been addressed since the early studies.^{2,3} We report here a combination of laser-flash photolysis (LFP) kinetic measurements, computations, and thermochemical analysis that provides this information. The kinetics and equilibrium between radicals **4** and **5** were also

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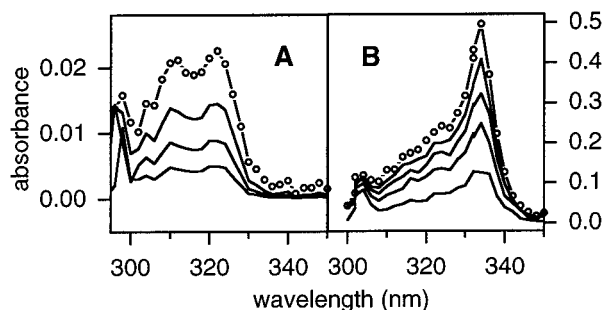
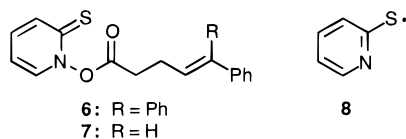


Figure 1. Time-resolved spectra showing formation of **4** and **1** following irradiation of **7** and **6**, respectively. (A) Traces from irradiation of **7** at 60, 100, 180, and 500 ns with data at 20 ns subtracted to give a baseline. (B) Traces from irradiation of **6** at 34, 54, 74, 94, and 134 ns with data at 14 ns subtracted to give a baseline. The symbols in the late-time spectra show the monitoring wavelengths.

addressed by the same approach in order to place the values obtained for the diphenyl-substituted system in context.

Results

Direct Kinetic Studies. Direct studies of the cyclizations of radicals **2** and **5** were measured by conventional LFP methods employing the PTOC ester^{9,10} radical precursors **6** and **7**, both of which were prepared from the corresponding known carboxylic acids, from reaction of the acid chlorides with the sodium salt of *N*-hydroxypyridine-2-thione.¹⁰ Because PTOC esters are thermally unstable and sensitive to UV light, compounds **6** and **7** were characterized only by NMR spectroscopy. PTOC esters are excellent radical sources for LFP studies because they have a strong long-wavelength absorbance at λ_{max} about 360 nm and are efficiently cleaved by 355 nm light from a Nd:YAG laser.¹¹ These features require dilute solutions of precursors in LFP studies and the use of a flow-cell assembly. The initial homolysis of **6** or **7** gives an acyloxyl radical, which decarboxylates rapidly on the nanosecond time scale,¹² and the 2-pyridinethiyl radical (**8**). Radical **8** has a long wavelength absorbance with λ_{max} at 490 nm¹³ but does not absorb strongly between 310 and 350 nm, the region where the di- and monophenyl benzylic radicals **1** and **4** were expected to absorb.¹⁴



Following 355 nm laser irradiation of the PTOC esters **6** and **7**, the expected UV signals for radicals **1** and **4**, produced by 3-exo cyclizations of **2** and **5**, grew in smoothly. Benzylic radical **4** had maxima at 312 and 322 nm, and dibenzylic radical **1** had λ_{max} at 334 nm. Time-resolved spectra are shown in Figure 1. The spectrum in Figure 1A is in good agreement with that

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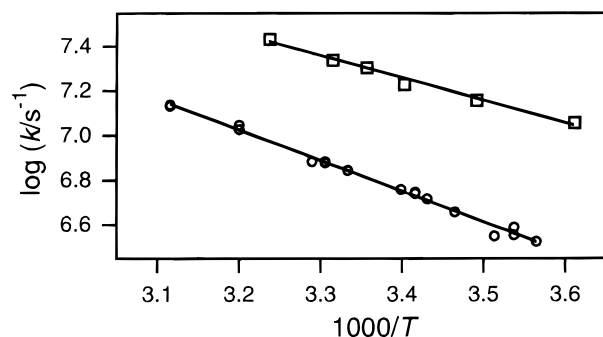


Figure 2. Rate constants for cyclization of radicals **2** (squares) and **5** (circles). The lines are the Arrhenius functions in Table 1.

Table 1. Temperature Dependent Functions for Cyclizations, Ring Openings, and Equilibria

reaction	temp dependent function ^a	$k_{(20)}$ or $K_{(20)}$ ^b	source
2 → 1	$(10.67 \pm 0.38) - (4.59 \pm 0.52)/\theta$	$1.7 \times 10^7 \text{ s}^{-1}$	this work, LFP
1 → 2	$12.3 - 12.4/\theta$	$1.1 \times 10^3 \text{ s}^{-1}$	this work, derived
2 ⇌ 1	$-1.6 + 7.8/\theta$	1.7×10^4	ref 3
5 → 4	$(11.41 \pm 0.19) - (6.26 \pm 0.26)/\theta$	$5.4 \times 10^6 \text{ s}^{-1}$	this work, LFP
4 → 5	$13.3 - 11.4/\theta$	$6.1 \times 10^4 \text{ s}^{-1}$	this work, derived
5 ⇌ 4	$-1.9 + 5.1/\theta$	80	ref 5
10 → 9	$12.1 - 11.1/\theta$	$6.5 \times 10^3 \text{ s}^{-1}$	see text
9 → 10	$(13.04 \pm 0.10) - (6.99 \pm 0.09)/\theta$	$6.6 \times 10^7 \text{ s}^{-1}$	ref 29
10 ⇌ 9	$-0.94 - 4.11/\theta$	1.0×10^{-4}	this work, derived

^a Log k for rate constants or log K for equilibria. Stated errors are 2σ . $\theta = 2.3RT$ kcal/mol. ^b Rate or equilibrium constant at 20 °C.

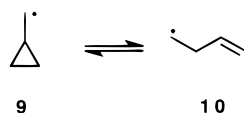
previously described for radical **4** formed “instantly” from photolysis of a benzene solution of di-*tert*-butyl peroxide and benzylcyclopropane.⁴

Kinetics of the cyclizations were studied over a temperature range of 4–48 °C. The results are listed in the Supporting Information and shown graphically in Figure 2. Both cyclizations are reversible, but the cyclic products are strongly favored at equilibrium, and cyclization of radical **2** to give radical **3** is about 2 orders of magnitude slower than cyclization of **2** to **1** (see below). Therefore, the observed kinetics are only those for the cyclization reactions. Arrhenius parameters for the cyclizations are collected in Table 1 along with other rate constants and equilibrium constants discussed later. At 20 °C, the ring-closure rate constants are $1.7 \times 10^7 \text{ s}^{-1}$ for **2** and $5.4 \times 10^6 \text{ s}^{-1}$ for **5**.

With the precise LFP-determined rate constants for cyclization of radicals **2** and **5** to radicals **1** and **4**, respectively, rate constants for the corresponding ring-opening reactions can be calculated from temperature-dependent functions for the equilibrium constants. Such a function for equilibration of radicals **1** and **2**, derived in the original study of this system,³ is listed in Table 1. A function for the equilibration of radicals **4** and **5** can be computed from the results of Beckwith and Bowry, who determined rate constants for both reactions by nitroxyl radical trapping,⁵ and this is also listed. Table 1 also contains the temperature-dependent functions for the parent radical system (**9** and **10**). The Arrhenius function for ring opening of radical **9** was recently modified to incorporate refined values for the kinetics of H-atom transfer from reactive trapping agents.¹⁵ The Arrhenius function for cyclization of **10** derives from competi-

(15) Newcomb, M.; Choi, S. Y.; Horner, J. H. *J. Org. Chem.* **1999**, *64*, 1225–1231.

tive deuterium scrambling studies of the homoallyl radical¹⁶ and has been corrected for the now accepted values for Bu_3SnH trapping of primary alkyl radicals.¹⁷

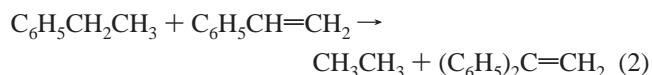
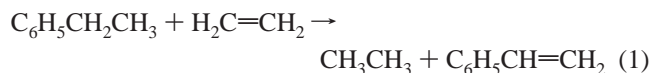


Thermochemical Analysis. A thermochemical analysis of the unsubstituted, monophenyl-substituted, and diphenyl-substituted radical systems was performed to evaluate the consistency of the temperature-dependent functions for the equilibrium constants in Table 1. From the bond dissociation energies (BDEs) of methane, ethane, toluene, phenylethane, diphenylmethane, and 1,1-diphenylethane,¹⁸ phenyl group substitution results in a radical stabilization of 15–16 kcal/mol, and substitution of a second phenyl group provides an additional 4–7 kcal/mol stabilization (Table S15 in the Supporting Information). Some inconsistency is apparent in the measured values; we employ BDE values of 101 kcal/mol for ethane, 88.5 kcal/mol for toluene, 86 kcal/mol for phenylethane, 82 kcal/mol for diphenylmethane, and 80 kcal/mol for diphenylethane for our analysis.

In comparison to a methyl group, a cyclopropyl group also stabilizes a radical center. In the cyclopropylcarbinyl radical, this stabilization is about 3 kcal/mol as determined from both measured (Table S15)¹⁸ and high-level G2¹⁹ computed BDE values for ethane and methylcyclopropane; the G2 results are 100.8 and 98.0 kcal/mol, respectively.²⁰ The physical basis for this stabilization is provided by low-temperature ESR studies of the rotational barrier in **9** (2.7 kcal/mol)⁶ and by three reasonably sophisticated calculations of that barrier (3.3–3.5 kcal/mol).⁸ In the case of radicals **1** and **4**, the well-known effect of “saturation” will attenuate the cyclopropyl group stabilization. In addition, our B3LYP/6-31G* calculations indicate that the minimum-energy conformation of **1** has the ring twisted about 47° from the bisected structure,²¹ unlike radicals **9** and **4** which have “bisected” minima. Overall, we assume a 3 kcal/mol stabilization by the cyclopropyl group in **9**, a 2 kcal/mol stabilization in **4** and a 1 kcal/mol stabilization in **1**. This gives net stabilizations of the phenyl groups of 14 kcal/mol for **9** → **4** and 5 kcal/mol for **4** → **1**.

The effect of phenyl substitution on the stability of ring-opened radical **5** was evaluated with the isodesmic reaction in eq 1. From heats of formation,²² the phenyl group stabilizes the double bond by 4.4 kcal/mol. Offsetting this quantity against the estimated radical-center stabilization of 14 kcal/mol in radical **4** results in the estimate that the net effect of phenyl-substitution should be to favor radical **4** over radical **5** by 10

kcal/mol in comparison to the unsubstituted radicals. Because the homoallyl radical (**10**) is favored by 4.1 kcal/mol over the cyclopropylcarbinyl radical (**9**) (Table 1), the enthalpic preference for cyclic radical **5** over radical **4** should be about 6 kcal/mol, in good agreement with the value of 6.3 kcal/mol in Table 1.



The effect of the second phenyl ring on the stability of the double bond in the acyclic radical **2** should be smaller. Unfortunately, consistent thermochemical data for the isodesmic reaction in eq 2 are not available.^{23,24} We estimated the incremental stabilization of the second phenyl group by computing the relative energies for the processes in eqs 1 and 2. Results are given in the Supporting Information. The calculations consistently overestimated the effect of monophenyl substitution, but B3LYP/6-31G* calculations, B3LYP/cc-pVTZ(-f) calculations, and high-quality localized MP2/cc-pVTZ(-f)²⁵ calculations showed a much smaller role for the second substitution. Assuming that the differential stabilization of the second phenyl group in the alkenes is 2 kcal/mol, **1** should be stabilized relative to **2** by 3 kcal/mol more than is **4** relative to **5**, in good agreement with the enthalpic difference of 2.7 kcal/mol between the corresponding temperature-dependent functions for the equilibria in Table 1.

Indirect Kinetic Studies. Radicals **1** and **2** were produced from their respective *tert*-butylperoxy esters **11** and **12** in the presence of trapping agents, and both “in-cage” and “out-of-cage” radical-derived products were characterized³ (see the scheme in the Supporting Information). Scheme 1 shows the reactions and products from diffusively free radicals. Peroxy ester **12** had a half-life of 150 min at 110 °C, whereas **11** had a half-life of about 100 min at 25 °C; therefore, studies from the two radical sources at a common temperature were not possible. Complex mixtures were obtained with the relatively poor hydrogen atom donor, 1,4-cyclohexadiene, apparently because of production of high concentrations of labile 1,4-cyclohexadienyl radicals that reacted by recombination and disproportionation with radicals produced in the peroxy ester fragmentation. Nonetheless, the product ratios could be accounted for computationally with reasonable assumptions.³ Details of the product studies are given in the Supporting Information.

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(19) The G2 (Gaussian-2) method was found to give a mean absolute error of only 1.3 kcal/mol for a test set of 125 well-characterized energy differences; see: Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Phys. Chem.* **1990**, *94*, 7221–7230.

(20) Schlegel, H. B. Private communication of unpublished results. We are grateful to Prof. Schlegel for providing us with this information.

(21) The structure of **1** was originally computed by Prof. K. N. Houk and D. Sawicka to whom we are grateful: Houk, K. N.; private communication to JDR 1998.

(22) *CRC Handbook of Chemistry and Physics*, 79th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, 1998; pp 5-5 to 5-60.

(23) Thermochemical estimates vary considerably. For example, Fischer and co-workers used measured and assumed values for BDEs and heats of formation to estimate the exothermicities of methyl radical additions to alkenes. Comparisons between (i) additions to ethene and styrene and (ii) additions to styrene and 1,1-diphenylethene are germane to the thermochemistry we are attempting to address. Differences of 10.7 and 2.5 kcal/mol for processes i and ii, respectively, were reported in 1995 (Wu, J. Q.; Fischer, H. *Int. J. Chem. Kinet.* **1995**, *27*, 167–179), in good agreement with the thermochemical differences we discuss. In ref 24, however, the same differences were listed as 11.7 and 7.9 kcal/mol, respectively. The latter value appears to be out of line; it can be traced mainly to a difference of about 6 kcal/mol in the estimated values for the heat of formation of 1,1-diphenylethene used in the two works.

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Scheme 1

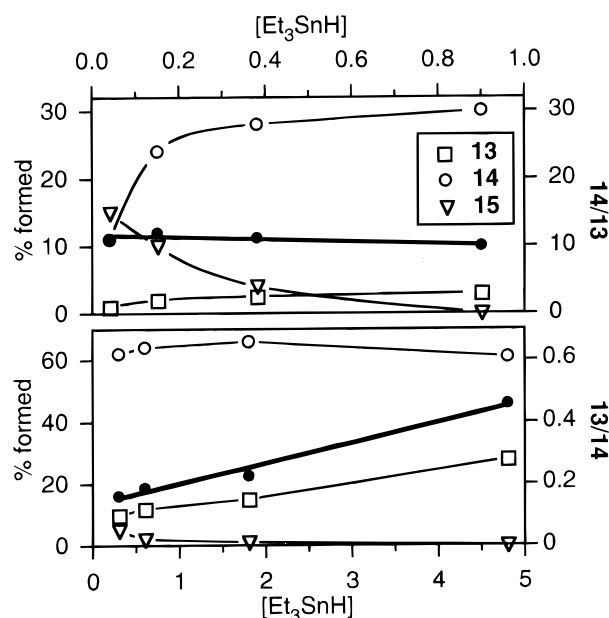
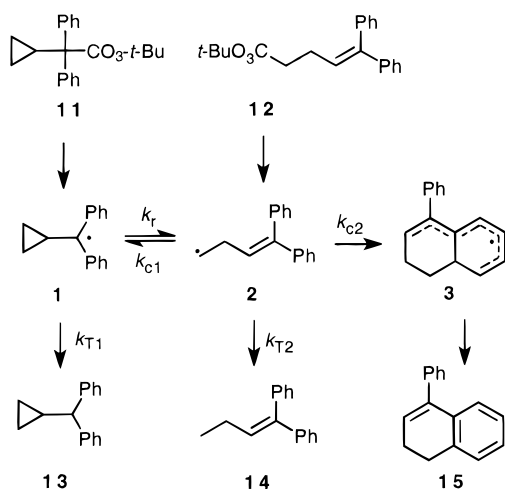


Figure 3. (A, top) Product yields from reaction of peroxyester **12** at 110 °C in the presence of Et_3SnH ; the solid circles are the ratios for $[\mathbf{14}]/[\mathbf{13}]$ (right axis), and the thick line is the regression fit for this ratio. (B, bottom) Product yields from the reaction of peroxyester **11** at 35 °C in the presence of Et_3SnH ; the solid circles are the ratios for $[\mathbf{13}]/[\mathbf{14}]$ (right axis), and the thick line is the regression fit for this ratio.

Results of trapping studies with the reactive trapping agent Et_3SnH were more readily analyzed. Good to high yields of products **13–15** were obtained in the presence of the tin hydride (Tables S10 and S11 in the Supporting Information). As shown in Scheme 1, these are the ultimate products from reactions of diffusively free radicals. In the plots in Figure 3, the linear ratios of products **13** and **14** as a function of tin hydride concentration with nonzero intercepts suggest that the equilibration reactions between radicals **1** and **2** were competitive with tin hydride trapping. That the yield of product **15** rapidly decreased as the concentrations of tin hydride increased indicates that cyclization of radical **2** to radical **3** is considerably slower than cyclization of **2** to **1**.

In principle, the relative rate constants from an equilibrating radical system such as **1** and **2** with trapping of both components can be obtained from the product distributions shown in Figure

3.²⁶ In practice, the data from decomposition of peroxy ester **12** are not useful, however. The ratio of products **14** to **13** decreased as the tin hydride concentration increased (Figure 3A); this is not possible unless alkene **14** was consumed in a secondary reaction. We assume that hydrostannation occurred at the elevated temperatures, resulting in loss of **14**.

At the lower temperatures involved in the thermolyses of peroxy ester **11**, product destruction in secondary reactions apparently was not a problem. The ratio of products $(\mathbf{13}/\mathbf{14})$ increased smoothly as a function of tin hydride concentration (Figure 3B). Equation 3 describes the kinetics where the rate

$$(\mathbf{13}/\mathbf{14}) = (k_{\text{T1}}^{\text{SnH}} k_{\text{c1}}/k_{\text{T2}}^{\text{SnH}}) + (k_{\text{T1}}^{\text{SnH}}/k_{\text{c1}})[\text{Et}_3\text{SnH}]_m \quad (3)$$

constants listed are those in Scheme 1 and $[\text{Et}_3\text{SnH}]_m$ is the average concentration of tin hydride.²⁶ Using the slopes of the $(\mathbf{13}/\mathbf{14})$ ratios at 35 and 10 °C (Table S11 in the Supporting Information) gives the Arrhenius function for Et_3SnH trapping of radical **1** relative to ring opening shown in eq 4. Division of

$$\log((k_{\text{T1}}^{\text{SnH}}/k_{\text{c1}})/\text{M}^{-1}) = -4.62 + 4.61/\theta \quad (4)$$

the intercepts by the slopes at each temperature gives the Arrhenius function for Et_3SnH trapping of radical **2** relative to cyclization shown in eq 5. Combining the relative Arrhenius

$$\log((k_{\text{T2}}^{\text{SnH}}/k_{\text{c2}})/\text{M}^{-1}) = -1.80 + 1.68/\theta \quad (5)$$

functions in eqs 4 and 5 and the absolute Arrhenius functions for ring opening of radical **1** and cyclization of **2**, respectively, one computes the absolute Arrhenius functions for reactions of Et_3SnH with the two radicals that are given in eqs 6 and 7. The values for reaction of radical **2** with Et_3SnH are similar to those for reactions of alkyl radicals with Bu_3SnH ,¹⁷ indicating that the results are reliable. The rate constant for reaction of Et_3SnH with radical **1** at 20 °C is $70 \text{ M}^{-1} \text{ s}^{-1}$.

Et_3SnH reaction with **1**:

$$\log(k_{\text{T1}}/\text{M}^{-1} \text{ s}^{-1}) = 7.65 - 7.8/\theta \quad (6)$$

Et_3SnH reaction with **2**:

$$\log(k_{\text{T2}}/\text{M}^{-1} \text{ s}^{-1}) = 8.9 - 2.9/\theta \quad (7)$$

Relative rate constants for cyclization of radical **2** to radical **3** in competition with trapping of **2** were obtained as follows. Plots of $\mathbf{15}/\mathbf{14}$ versus the inverse of the concentration of trapping agent give the ratio $(k_{\text{c2}}/k_{\text{T2}})^{26}$ if radical **3** gives product **15** exclusively. From the studies with peroxy ester **11** reacting in the presence of Et_3SnH (Table S11 in the Supporting Information), the slopes are (0.019 ± 0.004) and $(0.016 \pm 0.001) \text{ M}$ at 10 and 35 °C. Assuming a value of 0.018 M at 20 °C and combining this with eq 5, one calculates relative rate constants for the two cyclization reactions of radical **2** of $(k_{\text{c1}}/k_{\text{c2}}) = 200$ at 20 °C or $k_{\text{c2}} = 0.9 \times 10^5 \text{ s}^{-1}$ at 20 °C. Radical **3**, however, also yields additional products that appear to include 1-phenyltetrahydronaphthalenes. If we include trapping studies with 1,4-cyclohexadiene and estimated conversion efficiencies of ca. 35% for both reactions (see the Supporting Information), we calculate an Arrhenius function for cyclization of **2** to **3** that gives $k_{\text{c2}} = 1.4 \times 10^5 \text{ s}^{-1}$ at 20 °C (eq S11 in the Supporting Information).

Quantum Chemical Calculations. Table 2 lists calculated energies and enthalpies for the cyclizations of radicals **2** and **5**

Table 2. Calculated Relative Energies and Entropies of Interconversion at B3LYP/6-31G* Geometries

conversion	relative energy (kcal/mol)			rel entropy (eu)	
	B3LYP/ 6-31G*	B3LYP/ cc-pVTZ(-f)	Table 1	B3LYP/ 6-31G*	Table 1
10 ⇌ 9	2.26	4.05	4.1	-3.18	-4.3
5 ⇌ 4	-5.79	-4.18	-5.1	-4.44	-8.7
2 ⇌ 1	-8.24	-6.15	-7.8	-5.41	-7.3

and the parent radical, 3-butenyl (**10**). The B3LYP/6-31G* results are not definitive, but such calculations perform reasonably well for the unsubstituted system in comparison to ones carried out at much higher levels of theory.⁸ Comparison of the B3LYP/6-31G* value for cyclization of **10** with the experimentally determined enthalpic preference of 4.1 kcal/mol shows that the calculation overestimates the stability of the cyclopropylcarbinyl radical by 1.8 kcal/mol. If the same "overstabilization" is assumed for the mono- and diphenyl systems, the adjusted predictions for the enthalpies of **4** relative to **5** and of **1** relative to **2** become -4.0 and -6.4 kcal/mol, respectively, in qualitative agreement with the experimental values in Table 1. The larger-basis B3LYP/cc-pVTZ(-f) calculations gave a similar level of agreement more directly. Each set of calculations predicts a large change in reaction enthalpy for monophenyl substitution followed by a much smaller change for substitution of the second phenyl group.

The entropy differences obtained from the B3LYP/6-31G* vibrational analysis, a level of theory found suitable for assessing vibrational corrections,²⁷ also parallel those inferred experimentally, though the calculations do not support the large experimental value for the **5** → **4** conversion. The consistent underestimation of the entropy differences by the theoretical calculations may be due, at least in part, to the failure of the standard formulas to recognize the large contribution to the entropy from the nearly free rotation of the terminal methylene group in the ring-opened radicals.²⁸

Higher-order calculations on radicals **9** and **10** at their B3LYP/6-31G* geometries were performed using Gaussian 94 in an attempt to characterize the thermochemistry further. As would be done in an additive scheme such as G2,¹⁹ we estimated the enthalpy of interconversion for **10** → **9** as shown in eq 8

$$\Delta E = \Delta E(\text{large-basis MP2}) + \Delta E(\text{small-basis MP3} + \text{MP4 corrections}) + \Delta E(\text{ZPE}) + \Delta H_{\text{vib}} \quad (8)$$

where the last term is the thermal enthalpy associated with populating vibrational energy levels above the ground state (Table 3). This approach gave a computed enthalpy of interconversion (4.53 kcal/mol) in reasonable agreement with the experimental value of 4.1 kcal/mol. Despite the agreement, the calculation was sobering because it contained major contributions from relatively costly third-order (1.83 kcal/mol) and fourth-order (0.73 kcal/mol) perturbative corrections. Moreover, the spin-projected MP2 contribution was a poor estimate and even had the wrong sign for the small 6-31G* basis. The vibrational corrections for the parent system were small, but they would be larger for the monophenyl ($\Delta E(\text{ZPE}) = 1.57$ kcal/mol, $\Delta H_{\text{vib}} = -0.64$ kcal/mol) and diphenyl ($\Delta E(\text{ZPE}) = 1.98$ kcal/mol, $\Delta H_{\text{vib}} = -0.69$ kcal/mol) systems. Unfortunately,

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Table 3. Calculated Energy Components for Isomerization of Radical **10** to Radical **9**

calculation	$E(\mathbf{10}) - E(\mathbf{9})^a$
$\Delta\text{PMP2/cc-pVTZ}(-f)^a$	1.61
$\Delta\text{PMP2/6-31G}^*a$	-0.38
$\Delta\text{PMP4}(\text{SDQT})/6-31\text{G}^*a$	2.18
$\Delta\text{ZPE}(\text{B3LYP/6-31G}^*)^b$	0.72
$\Delta H_{\text{vib}}(\text{B3LYP/6-31G}^*)^b$	-0.36
total ΔH^c	4.53

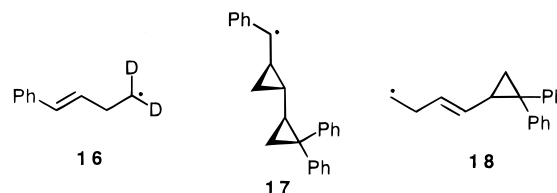
^a Computed using Gaussian 94 at Jaguar B3LYP/6-31G*-optimized geometries. ^b Computed using Jaguar v3.5 at restricted-open-shell B3LYP-optimized geometries. ^c $\text{PMP2/cc-pVTZ}(-f) + (\text{PMP4}(\text{SDQT})/6-31\text{G}^* - \text{PMP2/6-31G}^*) + \text{ZPE} + \Delta H_{\text{vib}}$; see text.

we were unable to address the larger systems by this approach because we could not obtain a full set of converged UHF wave functions with either Gaussian 94 or Gaussian 98.

Discussion

The LFP results provide precise, directly measured rate constants for cyclizations of radicals **2** and **5**. These values should also be quite accurate because they are much faster than diffusion-controlled radical-radical couplings and reactions of radicals with residual oxygen yet slow enough that convolution of the instrument response cannot be a factor. The major source of error most likely results from temperature fluctuations during the kinetic measurements.

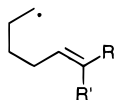
Kinetic data for the cyclization of radical **5** were previously reported in two studies. Bowry, Luszyk, and Ingold determined a rate constant for cyclization from the isotopic scrambling observed when **16** was generated in the presence of *n*-Bu₃SnH.⁴ Using the known rate constant for reaction of the tin hydride with a primary alkyl radical and assuming no isotope effect on the kinetics, they established a rate constant of $1.2 \times 10^7 \text{ s}^{-1}$ for cyclization of **16** (and thus of **5**) at 42 °C. Beckwith and Bowry reported the results of nitroxyl radical trapping studies conducted at temperatures between 42 and 80 °C; their results give rate constants for cyclization of **5** of $3.2 \times 10^6 \text{ s}^{-1}$ at 20 °C and $0.8 \times 10^7 \text{ s}^{-1}$ at 42 °C.⁵ The LFP results from this work give rate constants of $5.4 \times 10^6 \text{ s}^{-1}$ at 20 °C and $1.15 \times 10^7 \text{ s}^{-1}$ at 42 °C. The agreement between the LFP and tin hydride values is excellent; the factor of 1.4 difference between these values and the nitroxyl trapping results might reflect the necessity of assuming that the rate constants for reaction of radical **5** with the nitroxyl radical are equal to those for a model radical.⁵



The accuracy of the rate constants for ring openings of radicals **1** and **4** depends on the quality of the calculated equilibrium constants for these systems. The thermochemical analysis supports the values in Table 1, although not definitively, and the quantum calculations are in qualitative agreement. Further support for the accuracy of the derived equilibrium constants is found in the consistency of the derived entropic terms for the ring-opening reactions; the log A values are quite similar, as they should be because of the rigidity of these radicals.

The computed values for ring opening of **4** in Table 1 can be compared to those measured by nitroxyl trapping. Our derived rate constant for ring opening at 20 °C ($6 \times 10^4 \text{ s}^{-1}$) is smaller by a factor of 1.7 than that found by Beckwith and Bowry,⁵ about the same level of difference as found for the cyclization of **5** but in the opposite direction. An LFP study of another benzylic cyclopropylcarbonyl radical ring opening, that of radical **17**, appears to support our derived results. Radical **17** employs a "reporter-group"²⁹ for UV detection, and the reporter group is known to accelerate ring openings of cyclopropylcarbonyl radicals.³⁰ To gauge the extent of the acceleration in the endothermic ring opening of radical **17**, one can consider the effect of the same reporter group moiety in the endothermic cyclizations of radicals (*E*)- and (*Z*)-**18** which are 7–10 times faster at 20 °C than cyclization of the parent 3-butenyl radical.³¹ Assuming a similar acceleration for **17** and using the LFP value for ring opening of **17** at 20 °C of $4.6 \times 10^5 \text{ s}^{-1}$, one estimates a rate constant of $5\text{--}6 \times 10^4 \text{ s}^{-1}$ for ring opening of **4** at 20 °C, in agreement with the value in Table 1.

The kinetic effect of the phenyl substitution on the homoallyl radical cyclization is obviously enthalpy driven as one would expect, but the magnitude of the effect is noteworthy. The activation energies for addition of methyl radical to a large set of alkenes, reactions that are primarily enthalpy controlled, depend on the enthalpy of the reactions (h_r) with a proportionality constant of 0.20.²⁴ Considering only the additions of methyl radical to ethene, styrene, and 1,1-diphenylethene,²⁴ the dependence of E_a on h_r would be 0.24 to 0.29; the value is affected by the thermochemistry of the addition to diphenylethene.²³ For radicals **2**, **5**, and **10**, however, a plot of E_a versus h_r has a slope of 0.54, indicating that about half of the product stabilizations are manifested in the transition states. It would appear that the forming three-membered ring is an important feature because the rate constants for 5-exo cyclizations of radicals **19** (rate constants at 20 °C in units of s^{-1} are listed)^{15,26,32} show a dependence on relative enthalpy similar to that found in addition reactions of the methyl radical.²⁴



- 19a:** R = R' = H, $k = 2E5$
19b: R = Ph, R' = H, $k = 3E7$
19c: R = R' = Ph, $k = 4E7$

The other rate constants determined in this work were for cyclization of radical **2** to radical **3** and for reactions of Et_3SnH with radicals **1** and **2** (Scheme 1). The values for tin hydride trapping of the diphenylalkyl radical **1** (eq 6) should be useful because we are not aware of any previous report of the kinetics for reaction of a tin hydride with a diphenylalkyl radical. The tin hydride trapping of radical **1** must be nearly isothermic; our computed BDE for the hydrocarbon precursor to **1** is 79 kcal/mol, and the calculated BDE for Bu_3SnH based on corrections of photoacoustic calorimetry data is 78.6 kcal/mol.³³

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Conclusion

The relative rate constants for interconversion of radicals **1** and **2** estimated more than three decades ago from product analyses have been placed on an absolute kinetic scale. The temperature-dependent functions for kinetics and equilibria in Table 1 provide quantitative evaluation of the extent of phenyl group stabilization of a radical center and the resulting kinetic effects for both mono- and diphenyl-substituted cases. The results should serve as a useful standard for future computational studies that address the effects of phenyl substituents. Because the parent system radicals **9** and **10** are relatively small and well-characterized, one will be able to focus mainly on the effect of added substituents on derived species such as **1**, **2**, **4**, and **5**. Our investigations of these species were hindered because we found that converged spin-unrestricted wave functions for the α -phenyl-substituted radicals could not be reliably obtained using one of the most sophisticated computational approaches currently available.

Experimental Section

General Procedure for Preparation of PTOC Esters. The acid chloride was prepared by adding oxalyl chloride (1.5 equiv) to a solution of the carboxylic acid in benzene (0.05 to 0.1 M) containing a catalytic amount of DMF. After 1–2 h, the solvent and excess oxalyl chloride were removed under reduced pressure. The resulting acid chloride was taken up in benzene, and the solution was added to a stirred suspension of *N*-hydroxypyridine-2-thione sodium salt³⁴ in benzene containing a catalytic amount of DMAP. From this point on the reaction mixture was protected from light. After being stirred for 1–2 h, the reaction mixture was diluted with benzene, and the mixture was washed with 10% aqueous KHSO_4 solution, saturated aqueous NaHCO_3 solution, and brine. The benzene solution was dried over MgSO_4 , and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography to give the PTOC esters in about 65% yield.

5,5-Diphenyl-4-pentenoic Acid 2-Thioxo-2H-pyridin-1-yl Ester (6). By use of the general procedure, 5,5-diphenyl-4-pentenoic acid³⁵ (0.267 g, 0.0106 mol) gave **6**. ^1H (300 MHz): δ 2.63 (q, $J = 7.0$ Hz, 2 H), 2.84 (t, $J = 7.2$ Hz, 2 H), 6.15 (t, $J = 7.3$ Hz, 1 H), 6.61 (td, $J = 7.5$, 2.0 Hz, 1 H), 7.18, 7.42 (m, 11 H), 7.50 (d, $J = 5.7$ Hz, 1 H), 7.68 (dd, $J = 8.7$, 1.7 Hz, 1 H).

trans-5-Phenyl-4-pentenoic Acid 2-Thioxo-2H-pyridin-1-yl Ester (7). By use of the general procedure, *trans*-5-phenyl-4-pentenoic acid³⁶ (0.11 g, 0.0068 mol) gave **7**. ^1H NMR (300 MHz): δ 2.73 (q, $J = 7.2$ Hz, 2 H), 2.91 (t, $J = 7.2$ Hz, 2 H), 6.28 (dt, $J = 15.9$, 6.6 Hz, 1 H), 6.52 (d, $J = 15.9$ Hz, 1 H), 6.61 (td, $J = 6.9$, 2.0 Hz, 1 H), 7.18–7.38 (m, 6 H), 7.54 (d, $J = 5.4$ Hz, 1 H), 7.69 (dd, $J = 9.3$, 1.8 Hz, 1 H).

tert-Butyl diphenylcyclopropylperoxyacetate (11) was synthesized by adding 0.87 g of (100% excess) of powdered sodium *tert*-butyl peroxide to a stirred solution of 1.07 g (3.95 mmol) of diphenylcyclopropylacetyl chloride in 75 mL of pentane at -10 °C. The reaction mixture was maintained between -10 and 0 °C for 2 h. A sample withdrawn after 1.5 h had an infrared absorption at 1765 cm^{-1} in place of the carbonyl absorbance of the acid chloride at 1785 cm^{-1} indicating that the reaction had gone to completion. The pentane solution was filtered through a Celite bed and washed through with 50 mL of ice-cold pentane. The solution was concentrated under reduced pressure at 0 °C to about 3 mL and transferred to a small vessel with a nitrogen-inlet arm. The distillation flask was washed with 5 mL of pentane, and the resulting solution was added to that in the small vessel, upon which some white crystals formed. The vessel was flushed with nitrogen and cooled in several stages to -20 °C, whence crystallization appeared to be complete. The pentane solution was withdrawn under positive nitrogen pressure with a syringe. Fresh pentane was added, and the crystals were dissolved by warming on a steam bath for a minimal

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period; 15 mL of pentane were required to effect solution. On cooling to $-20\text{ }^{\circ}\text{C}$ and scratching, the crystals reformed. After 0.5 h at $-30\text{ }^{\circ}\text{C}$, the pentane solution was removed under positive nitrogen pressure. The solvent that adhered to the crystals was largely removed by maintaining the crystals in vacuo for 1 h at -10 to $0\text{ }^{\circ}\text{C}$. The yield was 0.53 g (38%). Relative to 10 aromatic protons, integration of the ^1H NMR spectrum at $-10\text{ }^{\circ}\text{C}$ in CCl_4 showed 3.8 broad secondary cyclopropyl protons much like those for the acid chloride, 9.2 *tert*-butyl methyl protons, an 0.8 proton singlet at $\delta \sim 2.1$, possibly due to water, and no olefinic proton resonances. A sample from another preparation melted with effervescence at ca. $65\text{ }^{\circ}\text{C}$ when heated rapidly. Analysis of active oxygen by iodide oxidation as described by Silbert and Swern³⁷ gave an average active oxygen content from two determinations of 94.5%.

***tert*-Butyl 5,5-diphenylperoxy-4-pentenoate (12)** was prepared by a modification of the method reported by Howden,³⁸ typically in 70% yield when prepared from 5 g of 5,5-diphenyl-4-pentenoic acid.³⁵ Samples of **12** had mp $40.5\text{--}42\text{ }^{\circ}\text{C}$ (lit.³⁸ mp $42\text{--}42.5\text{ }^{\circ}\text{C}$).

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LFP Kinetics. Kinetic measurements were carried out with an Applied Photophysics LK-50 laser kinetic spectrometer using the third harmonic (355 nm) of a Nd:YAG laser (7 ns pulse duration, 40 mJ/pulse). The flow system consisted of a jacketed addition funnel containing a fritted glass tube for helium sparging and attached by inert tubing to a UV cuvette. A temperature-regulated circulating bath was used to circulate fluid through the jacket of the funnel. Sample temperatures were measured by means of a copper–constantan thermocouple wire inserted into the interior of the cuvette through the sample outflow opening. Each kinetic trace contained 512 data points. For studies of **5**, 14 kinetic traces were summed to improve the signal/noise ratio. The impulse response of the system was measured to be $2.5 \times 10^8\text{ s}^{-1}$.

Indirect Kinetics. The experimental procedures have been reported.³ In brief, a small quantity (15–30 mg) of peroxyester **11** or **12**, an appropriate amount of Et_3SnH (prepared³⁹ by LAH reduction of the bromide), and cosolvent were sealed in tubes after freeze–thaw degassing. Following thermolysis in a controlled temperature bath, the tubes were opened, and the contents were analyzed by GC. Products **13–15** were identified by comparison of the GC retention times to those of authentic samples.

Computations. Quantum calculations for radicals **1**, **2**, **4**, **5**, **9**, and **10** were performed using *Jaguar* v3.5⁴⁰ or the *Gaussian* 94⁴¹ or 98⁴² series of programs. Calculations also were performed on unsubstituted, monophenyl-substituted, and 1,1-diphenyl-substituted ethanes and ethenes as model systems. Geometries were optimized using *Jaguar* at the restricted-open-shell B3LYP level of theory⁴³ using the 6-31G* basis set.⁴⁴ This level of theory is especially appropriate for determining the geometries of open-shell species because density functional calculations are less susceptible to geometry distortions resulting from spin contamination than are unrestricted Hartree–Fock (UHF)⁴⁵ calculations.²⁷ For the radical species, vibrational frequencies were also calculated at this level of theory to compute zero-point energies, thermal vibrational contributions to the enthalpy, and entropies. Better quality single-point energies were obtained using the larger and more flexible cc-pVTZ(-f) basis set.⁴⁶ Where feasible, Möller–Plesset correlation corrections to the UHF wave function were computed through fourth order⁴⁷ (singles, doubles, and quadruples), with spin projection⁴⁸ computed through third order.

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Supporting Information Available: Tables of product yields from thermal decompositions of peroxyesters, additional experimental details, and additional references (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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