Kinetic Studies of the Cyclization of the 6,6-Diphenyl-5-hexenyl Radical. A Test of the Accuracy of Rate Constants for Reactions of Hydrogen Transfer Agents[1]

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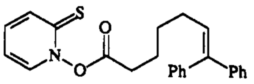
Cyclization of the 6,6-diphenyl-5-hexenyl radical (1) to the diphenylcyclopentylcarbinyl radical (2) was studied by indirect and direct methods. Indirect kinetic studies were accomplished by the PTOC–thiol method using hydrogen atom transfer trapping from thiophenol and from *tert*-butylthiol as the competing basis reactions over the temperature range of −47 to +44 °C. Tributyltin hydride trapping at 22 °C also was studied. There was excellent agreement in the rate constants for cyclization determined with the various trapping agents showing that the bimolecular rate constants for hydrogen transfer from these agents are equivalently placed on a kinetic scale. The Arrhenius function for cyclization of 1 was $\log (k_r/\mathrm{s}^{-1}) = 10.40–3.63/2.3RT$. In direct studies, radical 1 was produced by photolysis of the PTOC ester and the diacyl peroxide derived from 7,7-diphenyl-6-heptenoic acid. The rate constant for cyclization of 1 at 22 °C was 4.5×10^7 s^{-1}. The good agreement between the direct kinetic value and the value of 5.1×10^7 s^{-1} calculated from the above Arrhenius function confirms that the rate constants for hydrogen atom transfer from the trapping agents are accurate. The rate constant for cyclization of 1 at room temperature is about one-half as great as that for ring opening of the cyclopropylcarbinyl radical, and primary alkyl radical 1 should prove useful as a radical clock for timing fast radical reactions.

Unimolecular radical rearrangements have been widely applied in mechanistic probe studies where one searches for rearranged products as a qualitative indicator that radical intermediates were involved in a reaction and as radical clocks[2] in indirect kinetic measurements. The kinetics of the archetypal radical rearrangements, cyclization of the 5-hexenyl radical,[3] and ring opening of the cyclopropylcarbinyl radical[4] are generally considered to be accurately known and have been incorporated into many radical reaction rate constants via radical clock studies. Ironically, despite the fact that the rate constants of several radical rearrangements are probably quite precisely calibrated,[5] direct kinetic studies of a radical rearrangement involving bond reorganization have not been reported. In this paper we describe both indirect and direct kinetic studies of the cyclization of the 6,6-diphenyl-5-hexenyl radical (1). The results show that a variety of hydrogen atom transfer trapping agents available for indirect kinetic measurements of fast primary alkyl radical rearrangements are comparably calibrated and also accurate.

Radical 1 was chosen as a candidate for direct kinetic studies for several reasons. Whereas cyclization of the 5-hexenyl radical is too slow for accurate direct measurements in the absence of rigorous methods to assure that oxygen has been removed from the sample,[3] the diphenylethene moiety of 1 was expected to enhance the rate of cyclization substantially. In addition, the formation of a substituted diphenylalkyl radical upon cyclization of 1 to diphenylcyclopentylmethyl radical (2) was expected to give a species with a characteristic and readily identified UV spectrum. Finally, the insulation of the radical center in 1 from the functionality by three methylene groups assures that 1 will behave as a typical primary radical in indirect kinetic studies and other clock applications.

Results and Discussion

For the purpose of this study, radical 1 was produced by decarboxylation of the corresponding acyloxyl radical. Acyloxyl radical precursors were prepared from 7,7-diphenyl-6-heptenoic acid which was available from the monomethyl ester of adipic acid by conversion of the acid moiety to an aldehyde followed by a Horner–Emmons reaction to install the diphenylethene moiety. Indirect kinetic studies involved radical chain reactions of PTOC ester[6] 3. For direct studies, both 3 and diacyl peroxide 4 were employed.



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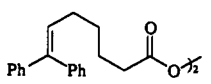

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Indirect Studies. Rate constants for cyclization of radical 1 to radical 2 were determined by the PTOC–thiol method (Scheme I).[7] In this indirect method, PTOC ester 3 reacted to give acyloxyl radical 5 which decarboxylated to give radical 1. The rearrangement of 1 to 2 competed

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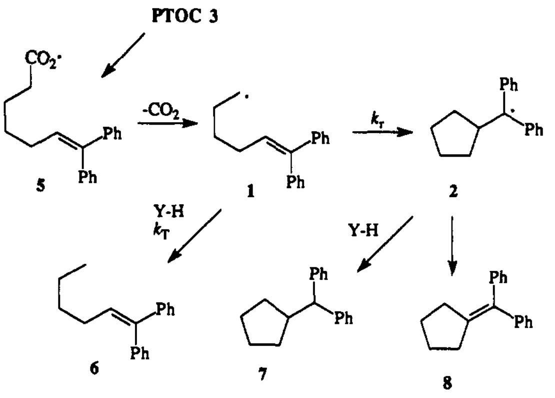
Scheme I



with bimolecular hydrogen atom transfer trapping by Y–H that gave acyclic hydrocarbon **6**. Rearranged radical **2** also reacted with the trapping agent to give cyclic product **7**. The Y• radical produced from the trapping agent reacted with PTOC ester **3** in a chain propagation step.

Kinetic studies of radical **1** cyclization in solvent THF were conducted over the temperature range of −47 to +44 °C using *tert*-butylthiol and thiophenol as trapping agents. Tributyltin hydride also was employed as a trapping agent at 22 °C. One reaction was conducted in acetonitrile, the solvent used for direct studies, in order to check the assumption that solvent effects on the kinetics of the radical reactions would be minor. The results are collected in Table I.

The total yields of products **6** and **7** were generally high, although yields were reduced somewhat at the lower reaction temperatures. With *t*-BuSH as a trapping agent, an additional product, identified by mass spectrometry as diphenylmethylenecyclopentane (**8**), was produced. One must conclude that the thiol was a relatively poor trapping agent for the stabilized radical **2** and that relatively high concentrations of this radical accumulated leading to radical–radical reactions. Such an effect should be more pronounced at lower temperatures because the velocity of photoinitiation (and therefore also of termination) was essentially constant in all reactions.

From the ratio of products **7**/**6**, the ratio of rate constants (k_r/k_T) could be calculated via eq 1 where $[\text{Y–H}]_m$ is the average concentration of the trapping agent. Equation 1

$$k_r/k_T = (\mathbf{7}/\mathbf{6})[\text{Y–H}]_m \qquad (1)$$

applies for cases where only products **6** and **7** were produced. However, in cases where radical–radical reactions were significant, it is likely that the stabilized radical **2** was selectively depleted and that the amount of cyclic product **7** was only a lower limit for the amount of radical **2** formed. Therefore, for reactions run at low temperatures (below 0 °C) with *t*-BuSH trapping, the ratio of cyclized to uncyclized product was calculated as (100 − %**6**)/%**6**.[8] The calculated values of k_r/k_T are included in Table I.

Rate constants for cyclization of radical **1** were calculated from the experimental k_r/k_T values with known values of k_T for each hydrogen atom donor;[9] these are given in the final column in Table I. Excellent agreement in the calculated k_r values was found for the PhSH and *t*-BuSH trapping results. Given the fast rate of cyclization of radical **1**, the kinetics of trapping by the less reactive agent Bu_3SnH were expected to be less precise; nevertheless, the calculated rate constant for cyclization of **1** at 22 °C based on tin hydride trapping was in good agreement with the values found with the other trapping agents. The PhSH and Bu_3SnH trapping kinetics were independently determined;[3,10] therefore, the correspondence of the values of k_r for radical **1** from studies using these two trapping agents shows that the two reagents are equivalently calibrated on a scale of reactivity. This conclusion is the same as that reached in the work resulting in the calibration of *t*-BuSH.[11]

The calculated k_r values for cyclization of radical **1** gave the Arrhenius function in eq 2 which is shown graphically in Figure 1. In eq 2, the errors shown in parentheses (2σ

$$\log (k_r/\text{s}^{-1}) = 10.40(11) - 3.63(14)/2.3RT \qquad (2)$$

for the final figure) are for the function and do not incorporate estimated errors in the rate constants for trapping. It is noteworthy that the log *A* value in eq 2 is quite similar to the log *A* value for cyclization of the parent radical, 5-hexenyl.[12] One would expect that the transition states for cyclization of **1** and the 5-hexenyl radical are similar, and the entropic terms in the Arrhenius functions should be nearly equal. The calculated rate constant for cyclization of **1** at 20 °C is 5.0×10^7 s^{-1}.

Direct Studies. Radical **1** was produced by two methods for direct studies. In one, the PTOC ester precursor **3** was irradiated with 355-nm light. Alternatively, the diacyl peroxide **4** was irradiated with 266-nm light. Both methods initially produced the acyloxyl radical **5** which decarboxylated to give **1**. There is little doubt that the lifetime of acyloxyl radical **3** is shorter than the 7-ns laser pulse.[13]

Experimentally, the formation of **1** was deduced from the ultimate presence of an intermediate identified as cyclic radical **2** by its UV spectrum. The insert in Figure 2 shows the UV spectrum of radical **2** which was present 94 ns after irradiation of diacyl peroxide **4** with 266 nm light. The absorbance centered at ca. 325 nm is similar to that observed for the diphenylmethyl radical.[15] When PTOC ester **3** was irradiated, the spectrum of **2** was observed to grow in with time (Figure 2), and the UV spectrum of a

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(8) The decision to adjust only the *t*-BuSH data below 0 °C might seem arbitrary. In fact, the yields of products **6** and **7** in the higher temperature reactions were so large that a similar adjustment of the ratios of **7**/**6** for these values had virtually no effect on the calculated Arrhenius function for cyclization.

(9) The k_T values for reactions of PhSH[10] (eq i) and of Bu_3SnH_3 (eq ii) are from direct laser-flash studies of reactions with primary radicals. The k_T values for *t*-BuSH[11] (eq iii) result from indirect studies that employed radical clocks. The k_T values for *t*-BuSH are derived from both the PhSH and Bu_3SnH values because the rate constants for the clocks employed in the thiol calibration were determined by trapping with PhSH and Bu_3SnH.

$$(\text{PhSH}) \log (k_T/\text{M}^{-1}\,\text{s}^{-1}) = 9.41 - 1.74/2.3RT \qquad \text{(i)}$$

$$(\text{Bu}_3\text{SnH}) \log (k_T/\text{M}^{-1}\,\text{s}^{-1}) = 9.1 - 3.7/2.3RT \qquad \text{(ii)}$$

$$(t\text{-BuSH}) \log (k_T/\text{M}^{-1}\,\text{s}^{-1}) = 8.37 - 2.0/2.3RT \qquad \text{(iii)}$$

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(12) The Arrhenius function for cyclization of the 5-hexenyl radical is ($\log k_r/\text{s}^{-1}$) = 10.4–6.85/2.3RT.[3]

(13) Rate constants for decarboxylation of acyloxyl radicals at room temperature range from 2×10^9 to 1×10^{10} s^{-1}.[14]

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Table I. Results of Trapping Studies of Radical 1[a]

Y–H	temp[b] (°C)	$[\text{Y–H}]_m$[c]	% yield 6	% yield 7	% yield 8	7/6[d]	k_r/k_T (M)	$10^{-7}k_r$[e] (s^{-1})
PhSH	44	1.93	77.2	20.8	*f*	0.27	0.52	8.4
	20	0.96	71.3	30.5	*f*	0.43	0.41	5.3
	20	1.44	75.4	20.4	*f*	0.27	0.39	5.0
	1	0.96	74	23.4	*f*	0.32	0.30	3.2
	1	1.44	77.6	16.5	*f*	0.21	0.31	3.2
	−20	1.93	75.5	10	*f*	0.132	0.26	2.0
	−20	2.57	75.4	6.7	*f*	0.088	0.23	1.8
t-BuSH	41	3.20	30	77	2	2.63	8.4	8.0
	41	3.84	31	64	1.3	2.10	8.1	7.7
	22	2.90	32.7	68	4.3	2.21	6.4	4.9
	22	3.94	38.5	54	3	1.48	5.8	4.5
	22	5.13	43.8	51	2	1.21	6.2	4.8
	2	2.90	33.9	58	4	1.82	5.3	3.2
	2	3.49	38.9	56	2.4	1.50	5.2	3.2
	−22	3.00	42	40	3	1.38[g]	4.1	1.8
	−22	4.73	52.2	30	3	0.92[g]	4.3	1.8
	−47	2.39	46	36.4	3	1.17[g]	2.8	0.77
	−47	2.52	48	28	6	1.08[g]	2.7	0.74
Bu_3SnH	22	1.85	7.9	88.1	*f*	11.2	21	4.7
	22	2.59	9.4	80.9	<1	8.6	22	5.0
t-BuSH[g]	22	3.53	34.5	58.3	1.5	1.73	6.1	4.7

[a] Reactions run in THF, initial PTOC **3** concentration was ca. 0.02 M. [b] ±1 °C. [c] Average concentration of donor. [d] Ratio of product **7** to **6**. [e] Rate constant for rearrangement calculated from k_r/k_T and k_T value from Arrhenius functions for hydrogen atom transfer trapping.[9] [f] Not detected. [g] Value of (100 − %**6**/%**6**) used. [g] Solvent was acetonitrile.

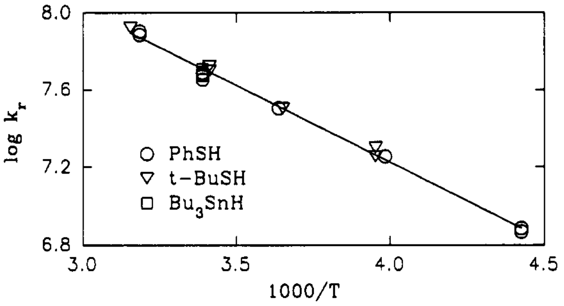

Figure 1. Temperature-dependent function for the rate constant for cyclization of radical 1. The rate constants are keyed to the basis trapping agent from which they derive by the symbols. The line is eq 2.

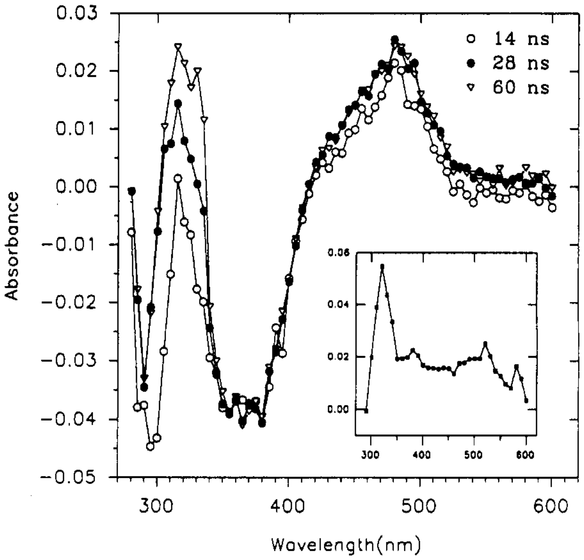

Figure 2. Time-resolved spectrum of transients produced by photolysis of PTOC ester 3 obtained 14, 28, and 60 ns after irradiation with 355-nm light. The growth in intensity in the 300–350-nm region follows an initial bleaching in the 290–400-nm region due to destruction of the PTOC ester. The inset shows the spectrum present 94 ns after photolysis of diacyl peroxide 4 with 266-nm light.

second intermediate, with an absorbance centered at 480 nm, was formed within the time period of the laser pulse. The latter absorbance resulted from the 2-pyridinethiyl radical which has been observed previously in laser flash studies with PTOC esters.[16] Further confirmation that the UV signal at 325 nm is correctly ascribed to radical 2 was obtained by observing the decay of the absorbance which was consistent with slow radical–radical reactions in nitrogen-purged samples (the initial pseudo-first-order decay rate constant was $k = 3 \times 10^5\ s^{-1}$) and a faster reaction with oxygen in samples saturated with oxygen (pseudo-first-order rate constant of $k = 9 \times 10^6\ s^{-1}$).

Attempted kinetic studies of the cyclization of radical 1 produced by 266-nm irradiation of diacyl peroxide 4 were complicated by a strong fluorescence. Although the spectrum of radical 2 was observed to grow in rapidly following the laser pulse, the precision of the kinetic measurements was poor. A crude rate constant in the range of 4–7 × $10^7\ s^{-1}$ at 22 °C was obtained.

When radical 1 was produced from PTOC ester 3 by irradiation with 355-nm light, fluorescence was not a problem, and precise kinetics could be measured. The kinetics of formation of radical 2 were measured at 2-nm increments from 310 to 342 nm. Figure 3 shows a portion of a kinetic trace. The kinetic results gave a rate constant for formation of radical 2 at (22 ± 1) °C of (4.5 ± 0.1) × $10^7\ s^{-1}$ (2σ). The measured rate constant is actually the sum of the first-order rate constant for cyclization of 1 and a pseudo-first-order rate constant for consumption of radical 1 in other processes (for example, reaction with oxygen). The pseudo-first-order processes are likely to be nonselective, and the velocity of these processes should be similar to that observed for loss of radical 2 in nitrogen purged samples. For a value of $k_{obs} > 1 \times 10^7\ s^{-1}$, these processes would be expected to contribute insignificantly to the velocity of the overall reaction, and they were ignored.

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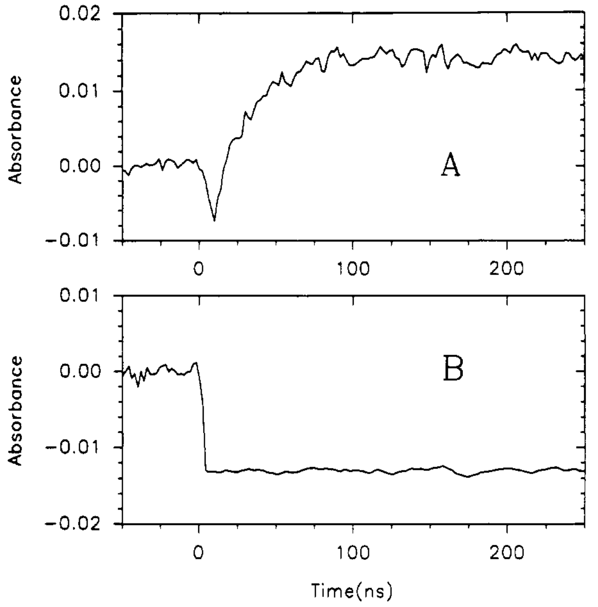

Figure 3. Plots of absorbance versus time (first 250 ns) following irradiation of PTOC ester **3** by a 7-ns laser pulse (time = 0) at 355 nm. (A) Absorbance at 326 nm showing growth of radical **2**. (B) Absorbance at 350 nm showing that bleaching was "instantaneous".

The calculated rate constant at 22 °C for cyclization of radical **1** from the Arrhenius function in eq 2 is $k = 5.1 \times 10^7$ s^{-1}. Agreement between the calculated rate constant and the experimentally measured rate constant is very good. This confirms that the rate constants for trapping of primary radicals by various H-atom donors are not only internally consistent but also accurate at least in the vicinity of room temperature. The rate constant for cyclization of radical **1** is about half that for ring opening of the cyclopropylcarbinyl radical;[4] because radical **1** is a "true" primary alkyl radical, it is possible that this radical rearrangement will find a number of clock applications.

Experimental Section

General. Reagents were purchased from Aldrich Chemical Co. unless noted. Tetrahydrofuran (THF) was distilled from potassium benzophenone under nitrogen immediately before use, acetonitrile was distilled from CaH_2 under nitrogen and stored over molecular sieves, and benzene was distilled from CaH_2 immediately before use. Thiophenol, *tert*-butylthiol, and tributyltin hydride were distilled and stored over molecular sieves.

^1H and ^{13}C NMR spectra were obtained at 300 and 75 MHz, respectively, on General Electric QE-300 and GN-300 spectrometers. Melting points were obtained on a Thomas Hoover capillary melting point apparatus and are uncorrected. Analytical GC was accomplished on Varian 3400 gas chromatographs equipped with flame ionization detectors; data were processed with computer-based chromatography software (Maxima 820, Waters Associates). Wide bore capillary SE 30 columns (Alltech) were used for GC separations. GC–mass spectrometry was accomplished with a Hewlett-Packard Model 5791 mass selective detector interfaced to an HP Model 5890 gas chromatograph; a 25-m × 0.25-mm SE-54 capillary column (Alltech) was employed. High-resolution mass spectrometry was performed by the Central Instrumentation Facility at Wayne State University.

Methyl 6-oxohexanoate was prepared as previously reported.[17]

Diethyl benzhydrylphosphonate was prepared by the method of Smith et al.[18] A mixture of 8 g (32.4 mmol) of benzhydryl bromide and 5.9 g (35.5 mmol) of triethyl phosphite was heated at reflux at 150 °C for 3 h under a still head until ethyl bromide ceased to distill. The residual viscous yellow oil was purified by silica gel chromatography (diethyl ether elution). Evaporation of the solvent under reduced pressure gave a white crystalline product (mp 40–41 °C) in 82% yield (8.1 g, 26.6 mmol): ^1H NMR ($CDCl_3$) δ 1.08 (t, $J = 7$ Hz, 6 H), 3.81 (m, 2 H), 3.95 (m, 2 H), 4.45 (d, $^3J_{HP} = 25$ Hz, 1 H), 7.21 (d, $J = 7.5$, 2 H), 7.29 (t, $J = 7.5$ Hz, 4 H), 7.54 (d, $J = 7.5$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 16.33 (d, $J_{CP} = 3.9$ Hz), 51.4 (d, $J_{CP} = 137$ Hz), 62.73 (d, $J_{CP} = 7$ Hz), 127.26, 128.70, 129.59 (d, $J_{CP} = 7.8$ Hz), 137.02 (d, $J_{CP} = 5.1$ Hz).

Methyl 7,7-diphenyl-6-heptenoate was prepared following the method of Newcomb et al.[19] To a mixture of 3 mL of 2.5 M *n*-BuLi (7.40 mmol) and 5 mL of THF at 0 °C was added dropwise a solution of 2.25 g (7.40 mmol) of diethyl benzhydrylphosphonate in 10 mL of THF. The ice bath was removed, and the mixture was stirred at room temperature for 1 h. To the resulting mixture was added dropwise a solution of 1.06 g (7.40 mmol) of methyl 6-oxohexanoate in 5 mL of THF. The mixture was stirred for 12 h and treated with saturated aqueous NH_4Cl solution. The mixture was separated, and the aqueous layer was washed with ether. The combined organic layers were dried with $MgSO_4$, and the solvent was removed under reduced pressure. The desired product was purified by column chromatography on silica gel (1:4 ether–hexanes elution). Evaporation of the solvent gave 1.52 g (70%, oil) of methyl 7,7-diphenyl-6-heptenoate: ^1H NMR ($CDCl_3$) δ 1.47 (m, 2 H), 1.60 (m, 2 H), 2.15 (q, $J = 7.5$ Hz, 2 H), 2.25 (t, $J = 7.5$ Hz, 2 H), 3.64 (s, 3 H), 6.06 (t, $J = 7.5$ Hz, 1 H), 7.19–7.40 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 24.49, 29.29, 29.34, 33.85, 51.42, 126.80, 126.85, 127.15, 128.11, 128.03, 129.33, 129.83, 140.12, 141.91, 142.65. This ester was previously reported without physical or spectral properties.[20]

7,7-Diphenyl-6-heptenoic acid was obtained by the hydrolysis of the ester. The above ester (1.14 g, 3.88 mmol), a solution of potassium hydroxide (2 molar equiv in 10 mL of water), and 10 mL of ethanol were placed in a 50-mL round-bottom flask equipped with a reflux condenser. The mixture was heated at reflux for 6 h. The basic solution was acidified with hydrochloric acid and extracted with ether. The organic phase was washed with saturated NaCl solution and dried with $MgSO_4$. Removal of the solvent at reduced pressure gave the desired acid in 96% yield (1.04 g, 3.71 mmol) which crystallized on standing: mp 63–64 °C (lit.[21] mp 72.5–73.5 °C, lit.[22] mp 70.5–71.5 °C); ^1H NMR ($CDCl_3$) δ 1.39 (m, 2 H), 1.50 (m, 2 H), 2.01 (q, $J = 7.3$ Hz, 2 H), 2.25 (t, $J = 7.3$ Hz, 2 H), 5.98 (t, $J = 7.3$ Hz, 1 H), 6.90–7.30 (m, 10 H), 10.40 (bs, 1 H); ^{13}C ($CDCl_3$) δ 24.09, 29.12, 29.25, 33.70, 126.71, 126.79, 127.04, 127.92, 128.03, 129.03, 129.70, 139.96, 141.93, 142.48, 179.68; high-resolution MS, calcd for $(M + 1)^+$ peak of $C_{19}H_{20}O_2$ 280.1463, found 280.1466.

1-[[(6,6-Diphenyl-5-hexenyl)carbonyl]oxy]-2(1*H*)-pyridinethione (3) was prepared by the standard method.[6,17] To a solution of the above acid (1.5 g, 5.36 mmol) in benzene (30 mL) were added dropwise thionyl chloride (0.96 g, 8.07 mmol, 1.5 molar equiv) and one drop of DMF. The reaction was heated at reflux for 2 h. The excess thionyl chloride was removed by azeotropic distillation with benzene. To a mixture of the sodium salt of *N*-hydroxypyridine-2-thione (Olin, 1.04 g, 6.97 mmol) and catalytic (15 mol %) DMAP in benzene was added dropwise the acid chloride. The heavy oil product was isolated by silica gel chromatography (1:1 ethyl acetate–hexanes elution) in 80% yield: ^1H NMR ($CDCl_3$) δ 1.58 (m, 2 H), 1.85 (m, 2 H), 2.17 (q, $J = 7.3$ Hz, 2 H), 2.72 (t, $J = 7.5$ Hz, 2 H), 6.10 (t, $J = 7.3$ Hz, 1 H), 6.63 (t, $J = 6$ Hz, 1 H), 7.05–7.41 (m, 11 H), 7.52 (d, $J = 7.1$ Hz, 1 H), 7.75 (d, $J = 8.4$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.83, 29.13, 29.21, 31.36, 112.52, 126.89, 126.95, 127.16, 128.07, 128.21, 128.92, 129.84, 133.48, 137.42, 137.58.

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Bis(7,7-diphenylhept-6-enoyl) peroxide (4) was prepared by the method of Beckwith et al.[4d] To a solution of 7,7-diphenyl-6-heptenoic acid (0.3 g, 1.07 mmol) in benzene (5 mL) was added oxalyl chloride (2 molar equiv) and 6 μL of DMF. The reaction mixture was stirred at room temperature for 1 h. Excess oxalyl chloride was removed under reduced pressure. The resulting acid chloride and finely powdered Na_2O_2 (1.2 molar equiv) in dry ether (10 mL) was treated with a small aliquot (0.5 mL) of water until the initially vigorous reaction subsided. The reaction mixture was washed with water, saturated aqueous $NaHCO_3$, and aqueous saturated NaCl and dried with $MgSO_4$. Removal of the solvent under reduced pressure gave 85% yield (>96% pure by NMR) of the desired diacyl peroxide product as an oil: ^{1}H NMR (CDCl$_3$) δ 1.59 (m, 4 H), 1.74 (m, 4 H), 2.20 (q, J = 7.2 Hz, 4 H), 2.41 (t, J = 7.2 Hz, 4 H), 6.15 (t, J = 7.2 Hz, 2 H), 7.18–7.48 (m, 20 H); ^{13}C NMR (CDCl$_3$) δ 24.21, 28.93, 28.99, 29.64, 126.85, 126.78, 127.06, 127.96, 128.09, 128.79, 129.71, 139.93, 142.12, 142.43, 168.91.

1,1-Diphenyl-1-hexene (6). PTOC ester **3** (55 mg, 0.141 mmol) was placed in a 10-mL shielded round-bottomed flask containing a stir bar. The flask was sealed with a septum and flushed with nitrogen. Dry degassed benzene (2.5 mL) and thiophenol (155 mg, 1.41 mmol) were added via syringe. The shield was removed, and the reaction mixture was irradiated at room temperature with a 150-W tungsten-filament lamp at a distance about 0.6 m for 1 h. The solvent was removed at reduced pressure. Chromatography of the crude product on silica gel (9:1 hexanes–ethyl acetate) gave 38 mg of a mixture containing 48% 1,1-diphenyl-1-hexene, 30% (diphenylmethyl)cyclopentane, and 22% phenyl 2-pyridyl disulfide as determined by ^{1}H NMR spectroscopy. The yield of 1,1-diphenyl-1-hexene was ca. 56%. The ^{1}H-NMR spectrum of **6** correlated well with the spectrum of 1,1-diphenyl-1-hexene reported by Köbrich et al.[23] ^{1}H NMR (CDCl$_3$) δ 1.2–1.5 (m, 6 H), 2.2 (q, J = 7.3 Hz, 2 H), 6.1 (t, J = 7.3 Hz, 1 H), 7.3 (m, 10 H); mass spectrum m/e (rel intensity) 236 (1, M$^+$), 194 (16), 193 (100), 178 (27), 165 (22), 115 (57), 91 (23).

(Diphenylmethyl)cyclopentane (7). PTOC ester **3** (40 mg, 0.103 mmol) was placed in a 10-mL shielded round-bottomed flask containing a stir bar. The flask was sealed with a septum and flushed with nitrogen. Dry and degassed benzene (3 mL) and 0.31 mmol of *tert*-butylthiol were added via syringe. The shield was removed, and the reaction mixture was irradiated at room temperature with a 150-W tungsten-filament lamp at a distance of ca. 0.6 m for 1 h. The solvent was removed at reduced pressure. Chromatography on silica gel (9:1 hexanes–ethyl acetate elution) gave 38.8 mg of a 1:1 mixture of **7** and *tert*-butyl 2-pyridyl disulfide as determined by ^{1}H NMR spectroscopy. The yield of **7** was ca. 87%: ^{1}H NMR (CDCl$_3$) δ 1.58 (m, 8 H), 1.70 (m, 1 H), 3.6 (d, J = 14 Hz, 1 H), 7.25 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ 25.32, 32.18, 44.44, 58.60, 125.81, 125.87, 127.91, 128.01, 128.1, 128.28, 128.88, 130.05; mass spectrum m/e (rel intensity) 236 (1, M$^+$), 168 (25), 167 (100), 166 (25), 152 (13). Compound **7** was previously prepared by reaction of benzhydryllithium with bromocyclopentane,[24] physical and spectral properties were not reported.

(Diphenylmethylene)cyclopentane (8) was identified by GC–mass spectrometry: m/e (rel intensity) 235 (1, M$^+$), 234 (100), 233 (22), 219 (10), 205 (43), 192 (24), 191 (39), 178 (14), 167 (36), 152 (12), 143 (12), 129 (24), 115 (22), 101 (5), 91 (20).

Indirect kinetic studies followed the methods previously described.[4c,11,17] In kinetic runs containing ca. 0.02 mmol of PTOC ester **3**, products **6** and **7** were identified by comparison of the GC retention times and, for selected samples, GC–mass spectral fragmentation patterns to those of the isolated samples. Product **8** was identified by its mass spectrum. Yields were determined relative to an internal standard of dodecane. GC response factors for products **6** and **7** were determined with authentic samples: the response factor for **8** was assumed to be equal to that of **7**.

Direct Kinetic Studies. Cyclization of the 6,6-diphenyl-5-hexenyl radical (**1**) was studied with an Applied Photophysics LK-50 kinetic spectrometer employing a Spectron Nd-YAG laser that supplied 266-nm (55 mJ) or 355-nm (70 mJ) light. Diacyl peroxide **4** solutions (ca. 1×10^{-4} M) in acetonitrile were studied in a 10- × 10-mm static cell. PTOC ester **3** solutions (ca. 8×10^{-5} M) in acetonitrile were studied in a 5- × 5-mm micro fluorimeter flow cell. Solutions were purged with nitrogen. In a typical experiment with **3**, a solution of the PTOC ester flowing through the cell was irradiated at 355 nm with a 7-ns laser pulse fired 100 ns after the onset of data collection. The change in optical density at a particular wavelength was then monitored over a 0.90-μs time interval with 2-ns resolution (512 total data points per trace). In a series of experiments, changes in optical density resulting from photolysis were monitored between 280 and 600 nm. In the region between 310 and 342 nm, a new signal consistent with that expected for the diphenylcyclopentylcarbinyl radical (**2**) was observed to grow in. In studies with the PTOC ester **3**, an additional signal between 420 and 500 nm was produced within the period of the laser pulse; a control experiment with the PTOC ester of undecanoic acid produced an essentially identical signal between 420 and 500 nm. A typical kinetic trace obtained from PTOC ester **3** at 326 nm is shown in Figure 3. The results of 17 kinetic determinations at 2-nm steps between 310 and 342 nm were combined by the weighted least-squares method[25] to give the measured rate constant.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of PTOC ester **3** and diacyl peroxide **4** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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