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Absolute Rate Constants for Iminyl Radical Reactions

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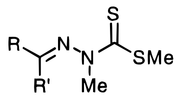
The kinetics of cyclization of the 2-methyl-6,6-diphenyl-5-hexeniminyl radical (**3**) were measured by laser flash photolysis methods from 0 to 50 °C, and the kinetics of trapping of radical **3** by thiophenol and *p*-chlorothiophenol were determined between 4 and 83 °C by indirect methods using the unimolecular rate constants as the basis values. Radical **3** cyclizes with a rate constant of $2.2 \times 10^6\ s^{-1}$ at 25 °C and reacts with thiophenol and *p*-chlorothiophenol at this temperature with rate constants of 0.6 and $1.4 \times 10^7\ M^{-1}\ s^{-1}$, respectively. Bu_3SnH reacted with **3** too slowly to prevent nearly complete cyclization, but a crude rate constant for the trapping reaction was estimated. The cyclization and trapping reactions of iminyl radical **3** are slower than the corresponding reactions of alkyl radicals.

Synthetic applications of radical-based methods are increasing rapidly. Nitrogen-centered radical reactions are not as prevalent as those of carbon radicals, but new entries to nitrogen radicals that can be employed in chain reactions are resulting in increased attention to these intermediates. Iminyl radicals are especially attractive intermediates due to their apparent high reactivity under strictly neutral conditions and the fact that they can be produced directly from several precursors or by addition of another radical to a nitrile group.[2,3] As with any radical intermediate employed in chain reactions, knowledge of the rate constants of iminyl radical reactions would be useful for synthetic design, but kinetic studies of iminyl radical reactions have been limited. The kinetics of iminyl radical self-trapping[4a] and *β*-fragmentations[4] have been reported. The cyclopentaniminyl radical has been shown not to open at ambient temperature,[3b] but a cyclopropaniminyl radical, formed as an intermediate in a 1,2-nitrile migration, must cleave rapidly.[3c]

Absolute kinetic measurements are obviously necessary for creating a kinetic scale for any type of radical. For cases where few or no basis reaction rate constants are available, the U.S. group has used a protocol wherein rate constants of unimolecular reactions producing benzylic or diphenylalkyl radical products are measured by laser flash photolysis (LFP) methods, and the radical clocks thus calibrated are used in either direct LFP or indirect competition kinetic reactions to measure the rate constants of second-order reactions.[5] The French group recently developed an entry to iminyl radicals via xanthic hydrazones **1** that react in radical chain reactions with Bu_3SnH (addition of $Bu_3Sn^{\bullet}$ to the thione sulfur followed by N−N homolytic cleavage),[6] and these radical precursors were expected to be photosensitive. We report here the combination of these two approaches for calibration of an iminyl radical clock and for measurements of rate constants for reactions of this iminyl radical with hydrogen atom transfer agents.



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Results and Discussion

Xanthic hydrazone **2**, produced from the corresponding ketone (prepared by standard methods, see the Experimental Section) in a simple condensation reaction, has been reported previously.[6] When **2** was allowed to react in the presence of Bu_3SnH with AIBN for radical chain initiation, pyrroline **5** was produced in 79% isolated yield (Scheme 1).[6] The reaction sequence resembles that of the

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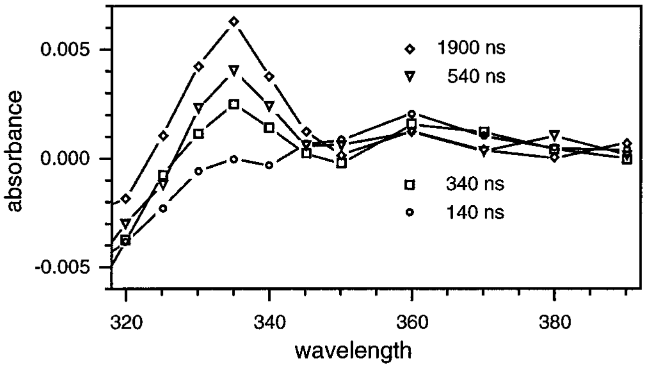


Figure 1. Time-resolved spectrum for radical **4**. Absorbances obtained at 140, 340, 540, and 1900 ns after the laser flash are shown.

Scheme 1

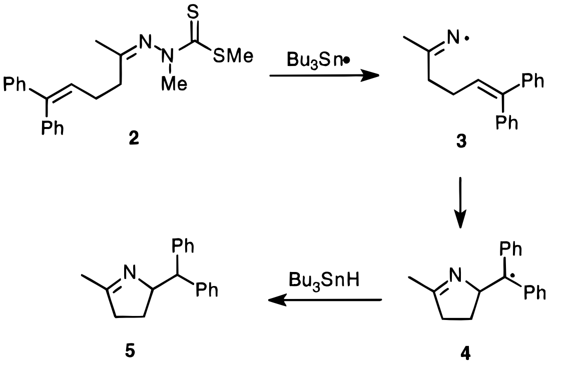


Table 1. Observed Rate Constants for Cyclization of Radical 3 to Radical 4.

T^a (°C)	$k_{obs} \times 10^{-6\,b}$ (s^{-1})	T^a (°C)	$k_{obs} \times 10^{-6\,b}$ (s^{-1})
−0.5	0.92 ± 0.07		3.09 ± 0.21
	1.00 ± 0.05		2.53 ± 0.23
10.6	1.32 ± 0.19	41.5	3.13 ± 0.44
	1.44 ± 0.10		3.20 ± 0.41
20.0	1.63 ± 0.23		3.43 ± 0.45
	1.74 ± 0.12	50.5	4.35 ± 0.40
30.8	2.59 ± 0.12		5.36 ± 0.47

[a] ± 0.2 °C. [b] Errors are 2σ.

important Barton–McCombie deoxygenation sequence, which employs xanthates and related thionocarbonyl derivatives of alcohols.[7]

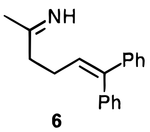
In LFP experiments, irradiation of **2** in THF with 266 nm light from a Nd-YAG laser was followed by growth of a weak signal with λ_{max} at about 335 nm. Figure 1 shows a time-resolved spectrum obtained from single laser flash experiments. The spectrum clearly indicates the formation of diphenylalkyl radical **4**, which was expected to have λ_{max} at about 330 nm.

The weak signal growth in the LFP experiments indicates a low efficiency for photocleavage of **2**. Nevertheless, reasonable kinetic traces were obtained by averaging several (up to 50) experiments for each run. Kinetics were measured between 0 and 50 °C, and the results are given in Table 1. Due to the low signal intensity, random errors were somewhat large; typical errors at 2σ were 5–10% of the absolute values. The cyclization of radical **3** to radical **4** is described by the Arrhenius function in eq 1 where the errors are 2σ and $\theta = 2.3RT$ kcal/mol. From eq 1, one calculates a rate constant for cyclization of **3** at 25 °C of 2.2×10^6 s^{-1}.

$$\log (k \times \mathrm{s}) = (10.3 \pm 0.4) - (5.4 \pm 0.6)/\theta \qquad (1)$$

The observed rate constants were in the range of $(1-5) \times 10^6$ s^{-1}, which is optimal for LFP studies with a ns kinetic spectrometer because potential interfering processes cannot have rate constants exceeding about 1×10^4 s^{-1}. In the direct study, one is observing formation of radical **4**, but the observed kinetics are for the loss of radical **3** by all of the processes, and one must be concerned with other possible pathways for loss of radical **3**. Oxygen concentrations of $<1 \times 10^{-6}$ M are obtained in our method, so pseudo-first-order reactions with oxygen cannot exceed 4×10^4 s^{-1}. The radical concentrations also must be $<1 \times 10^{-6}$ M on the basis of the very weak product signals; thus, diffusion-limited radical-radical reactions consuming **3** must occur with pseudo-first-order rate constants of $<2 \times 10^4$ s^{-1}. Other potential sources of UV intensity at 335 nm are intermolecular additions of either radical **3** or the nitrogen-centered byproduct radical from initial cleavage of substrate to another molecule of precursor **2**, but these reactions would have pseudo-first-order rate constants of about 1×10^4 s^{-1} if the bimolecular rate constants were unreasonably large (i.e., 1×10^8 M^{-1} s^{-1}) because the initial concentrations of **2** were about 1×10^{-4} M.

The kinetics of bimolecular reactions of radical **3** could be studied by competition methods. In principle, production of **3** in a radical chain process in the presence of a hydrogen atom transfer agent would give mixtures of imine **6** from trapping and pyrroline **5** from cyclization followed by trapping, and the rate constants for trapping could be calculated from the product distributions, the concentrations of trapping agent, and the rate constants for cyclization. In practice, the indirect kinetic studies were complicated for two reasons. Imine **6** was labile and rapidly hydrolyzed to the corresponding ketone. More problematical were the facts that a strongly thiophilic radical such as a stannyl radical was necessary to propagate the chain reaction by addition to precursor **2** but Bu_3SnH was found to react too slowly with **3** to prevent nearly complete cyclization of the radical (see below).



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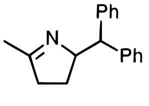

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Reactions of thiophenols with **3** were fast enough to trap this radical in competition with cyclization, but thiyl radicals will not propagate the chain reaction with precursor **2**. Thus, we were required to employ mixed hydride reagents of a thiophenol and Bu_3SnH for competition kinetic studies. The thiophenol reacts with either **3** or **4**, the thiyl radical thus formed reacts with Bu_3SnH, and the stannyl radical propagates the chain reaction by addition to precursor **2**. Similar "mixed hydride" reagents have been employed by Roberts[8ab] (Et_3SiH and *t*-BuSH) and Crich[8c] (Bu_3SnH and PhSeH) where the group 6 hydride is the fast radical-trapping agent and

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Table 2. Products from Reactions of 2 in the Presence of Thiophenols

thiol	T (°C)[a]	concn[b]	[**5**]/[**6**][c]	k_c/k_T[d] (M)
PhSH	4	0.30	0.42	0.17
		0.50	0.50	0.25
	30	0.30	1.16	0.35
		0.50	0.90	0.45
	50	0.30	1.70	0.51
		0.50	0.90	0.45
	80	0.30	1.94	0.58
		0.30	2.66	0.80
		0.50	1.59	0.80
		0.50	1.50	0.75
p-ClC$_6$H$_4$SH	8	0.27	0.43	0.12
		0.51	0.25	0.13
	38	0.30	0.55	0.16
		0.56	0.33	0.18
	63	0.26	0.99	0.26
		0.54	0.49	0.26
	83	0.29	1.17	0.34
		0.58	0.52	0.30

[a] ± 0.5 °C. [b] Mean concentration of thiol. [c] Ratio of products **5** to **6** determined by NMR for PhSH reactions and by GC for ClPhSH reactions. [d] Ratio of rate constants.

the group 4 hydride reacts with the group 6 radical to give a radical that can propagate a chain reaction. Typically, the group 6 hydride is employed in low concentration or even in a catalytic manner, and the Group 4 hydride is the sacrificial reductant, but we used relatively high concentrations of ArSH, which assured that the concentrations would be effectively unchanged over the course of the reactions.

Indirect kinetic studies of trapping of iminyl radical **3** by thiophenol and p-chlorothiophenol (ClPhSH) in cyclohexane were conducted over the temperature range 4−83 °C. For the PhSH reactions, the solvent was removed after the reaction, and the residue was dissolved in benzene-d_6 and analyzed by NMR spectroscopy. For the ClPhSH reactions, the crude reaction mixtures were partially purified by chromatography on silica gel, which effected hydrolysis of imine **6** to the ketone, and the product mixtures were analyzed by GC. For the latter procedure, repeated silica gel chromatography of the product mixture was shown not to alter the product ratio.

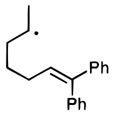
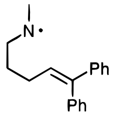
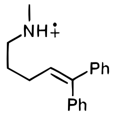
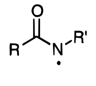
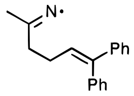
The results of the competition kinetic studies are given in Table 2. As one might expect on the basis of the relatively complicated handling procedures, random errors were large, especially in the case of the PhSH studies with NMR analyses. Most radical reactions are relatively insensitive to solvent effects,[9] and we make the logical assumption that the rate constants for cyclization of **3** are the same in cyclohexane and THF. Relative Arrhenius functions for the cyclization and trapping reactions were determined from the kinetic results and combined with the Arrhenius function for cyclization to give the temperature-dependent functions for trapping by PhSH in eq 2 and for trapping by ClPhSH in eq 3 where errors (at 2σ) have been propagated. The calculated rate constants for reactions of the two agents with **3** at 25 °C are 0.6 and 1.4 × 10^7 M^{-1} s^{-1}, respectively.

$$\log (k \times \mathrm{Ms}) = (8.5 \pm 0.6) - (2.3 \pm 0.9)/\theta \qquad (2)$$

$$\log (k \times \mathrm{Ms}) = (9.2 \pm 0.5) - (2.8 \pm 0.7)/\theta \qquad (3)$$

The parameters in the temperature-dependent functions for trapping are reasonable for fast second-order reactions, but the large errors prevent one from reaching any conclusions regarding differences in entropic and enthalpic effects. Nevertheless, the rate constants calculated from eqs 2 and 3 are considerably more precise than the errors in the functions might suggest due to the fact that log A and E_a are correlated. For example, the average difference between the calculated and mean experimental rate constants for reaction of PhSH at each temperature is 6%, and the calculated and mean experimental rate constants for reaction of ClPhSH at each temperature differ by only 3% on average. These differences are smaller than the ranges of the experimental values. Thus, p-chlorothiophenol clearly reacts faster with the iminyl radical than does thiophenol, by about a factor of 2 at 25 °C.

Table 3. Radical Rate Constants at 25 °C

Radical	k_c (s^{-1})	k_T PhSH (M^{-1} s^{-1})	k_T Bu$_3$SnH (M^{-1} s^{-1})
	2 × 10^7 (ref 5b)	1.0 × 10^8 (ref 10)	1.4 × 10^6 (ref 11)
	3 × 10^5 (ref 5d)	1.2 × 10^8 (ref 5d)	5 × 10^5 (ref 5d)
	ca. 1 × 10^{10} (ref 5c)	4 × 10^7 (ref 5c)	ca. 1 × 10^8 (ref 5c)
		8 × 10^7 (ref 12)	7 × 10^8 (ref 13)
	2 × 10^6	6 × 10^6	ca. 3 × 10^3

As noted earlier, Bu$_3$SnH reacted with **3** so slowly that nearly complete cyclization of the radical occurred. Nevertheless, a crude rate constant for Bu$_3$SnH trapping was obtained at 83 °C for reactions conducted with 1.6 and 3.3 M reagent; the trapping rate constant was ca. 2 × 10^4 M^{-1} s^{-1} at this temperature. If one assumes that the preexponential term in the Arrhenius function for this tin hydride reaction is the same as those observed in carbon radical-trapping reactions by Bu$_3$SnH[11] (log A = 9.2), then the estimated rate constant for Bu$_3$SnH reaction with **3** at 25 °C would be 3 × 10^3 M^{-1} s^{-1}. Because less than 1% trapping was observed in the Bu$_3$SnH experiments, these kinetic values are quite approximate and *should be employed only with caution*.

The amount of kinetic data available for nitrogen-centered radicals is rapidly increasing, and comparisons between various nitrogen-centered radicals and carbon radicals are useful for predicting trends in reactivity. Table 3 contains rate constants for cyclizations of a series of structurally similar radicals and for second-order

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reactions of these radicals with PhSH and Bu_3SnH. From inspection of the reactivities of the nitrogen radicals with the two hydrogen atom transfer agents, a contrast between the “nucleophilic” character of the aminyl and iminyl radicals and the “electrophilic” character of the aminium cation and amidyl radicals is apparent. Iminyl radical **3** cyclizes 1 order of magnitude less rapidly than the related carbon radical but also reacts less rapidly than a carbon radical with hydrogen atom transfer trapping agents, and one would predict that iminyl radicals formed in chain reaction sequences could prove to be as versatile as carbon radicals.

Experimental Section

Ethyl 3,3-Diphenylpropenoate. To a suspension of 60% sodium hydride (5.3 g, 0.132 mol; washed with three portions of anhydrous pentane) in anhydrous THF (150 mL) under an argon atmosphere was added triethyl phosphonoacetate (23.7 mL, 0.12 mol) in 50 mL of anhydrous THF. After the evolution of hydrogen gas had subsided, the solution was heated at reflux for 15 min. Benzophenone (10.9 g, 60 mmol) in anhydrous THF (50 mL) was then added, and the mixture was heated at reflux for 3 h, cooled, and poured into 200 mL of 1 N aqueous citric acid solution. The mixture was extracted with three portions of ether. The combined ether extracts were washed successively with water and brine and dried over sodium sulfate. The solvent was removed to afford an oil that was purified by distillation (14.83 g, 98%). Bp: 140 °C, 0.07 mbar (lit.[14] bp 157−158 °C, 3 Torr). ^1H NMR ($CDCl_3$): δ 1.11 (t, J = 7.3 Hz, 3 H), 4.05 (q, J = 7.3 Hz, 2 H), 6.37 (s, 1 H), 7.19−7.39 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ 18.84, 59.77, 117.38, 127.69, 127.90, 128.11, 128.87, 129.00, 129.20, 129.42, 129.84, 138.87, 140.63, 159.19, 165.80. IR (neat): $\nu = 1722, 1617\ cm^{-1}$.

3,3-Diphenyl-2-propen-1-ol. A slurry of $LiAlH_4$ (4.6 g, 0.121 mol) in dry ether (180 mL) was cooled to −75 °C before addition of a solution containing ethyl 3,3-diphenylpropenoate (15.3 g, 60.6 mmol) in dry ether (60 mL). The reaction mixture was stirred for 15 min at −45 °C before addition of ethyl acetate (70 mL) followed by 70 mL of water. After the mixture was warmed to room temperature, the organic layer was filtered, and the residue was washed with water and ether. The filtrate was extracted with ether, and the organic layer was dried over sodium sulfate. The solvent was removed to give a nearly quantitative yield (12.5 g) of a colorless oil that crystallized upon trituration with a mixture of pentane−ether. Mp: 57−59 °C (lit.[15] bp 153−155 °C, 0.5 Torr). ^1H NMR ($CDCl_3$): δ 1.54 (s, 1 H), 4.21 (d, J = 6.7 Hz, 2 H), 6.26 (t, J = 6.7 Hz, 1 H), 7.16−7.38 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ 60.43, 127.49, 127.60, 127.69, 127.80, 128.16, 128.47, 129.72, 139.06, 141.82, 143.73. IR (neat): $\nu = 3344\ cm^{-1}$.

6,6-Diphenyl-5-hexen-2-one. 3,3-Diphenyl-2-propen-1-ol (1.00 g, 4.76 mmol) and mercuric acetate (0.091 g, 0.24 mmol) were added to freshly distilled 2-methoxypropene (10 mL). The reaction mixture was heated at reflux for 24 h under an argon atmosphere, cooled, and then filtered through neutral alumina. Excess 2-methoxypropene and the methanol formed in the reaction were distilled under reduced pressure. The crude residue consisting of 1-(isopropenyloxy)-3,3-diphenyl-2-propene was taken up in distilled CH_2Cl_2 (5 mL), and the solution was treated with dried lithium perchlorate[16] (30 mg, 0.28 mmol). The mixture was stirred at room temperature for 3 h and then poured into ether. The mixture was washed with three portions of water, and the organic layer was dried over sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by flash chromatography on silica gel (ether/pentane 3:7) to yield 6,6-diphenyl-5-hexen-2-one (0.585 g, 49%) as a yellow oil which was used in the next step without further purification. ^1H NMR ($CDCl_3$): δ 2.09 (s, 3 H), 2.38 (dt, $J = J'$ = 7.2 Hz, 2 H), 2.53 (t, J = 7.2 Hz, 2 H), 6.02 (t, J = 7.2 Hz, 1 H), 7.15−7.38 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ 23.5, 29.13, 43.01, 126.36, 127.7, 129.1, 139.12, 141.7, 144.0, 207.31. IR (neat): $\nu = 1716\ cm^{-1}$.

***N'*-(6,6-Diphenyl-5-hexen-2-ylene)-*N*-(methylhydrazino)carbodithioic Acid Methyl Ester (2).** To a solution of 6,6-diphenyl-5-hexen-2-one (0.5 g, 2 mmol) in 2 mL of methanol were added *N*-methylhydrazinecarbodithioic acid methyl ester (0.53 g, 3 mmol) and acetic acid (2 mL). The mixture was stirred at room temperature for 12 h. The solvent was removed *in vacuo,* and the crude product was purified by flash chromatography on silica gel (ether/heptane, 2:8) to give **2** (0.47 g, 64%) as a yellow oil that solidified upon standing. Mp: 69−71 °C. ^1H NMR ($CDCl_3$): δ 1.8 (s, 3 H), 2.48 (s, 3 H), 2.52−2.60 (m, 4 H), 3.56 (s, 3 H), 6.16 (t, J = 7 Hz, 1 H), 7.15−7.43 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ 18.53, 19.29, 26.14, 38.33, 42.63, 127.24, 128.19, 128.38,128.50, 129.66, 129.83, 139.69, 142.15, 143.1, 180.8. IR (neat): $\nu = 1622, 1366, 1200, 1100\ cm^{-1}$. UV (THF): λ_{max} 252 nm, ϵ = 22 000; shoulder at λ 287 nm, ϵ = 11 600. Anal. Calcd for $C_{21}H_{24}N_2S_2$: C, 68.44; H, 6.56. Found: C, 68.42; H, 6.55.

3,4-Dihydro-5-(diphenylmethyl)-2-methyl-5*H*-pyrrole (5). A solution of Bu_3SnH (0.323 mL, 1.2 mmol) and AIBN (37 mg, 0.12 mmol) in a deoxygenated mixture of cyclohexane (2 mL) and toluene (2 mL) was added dropwise over 6 h to a refluxing solution of **2** (368 mg, 1 mmol) in deoxygenated cyclohexane (4 mL). The reaction, which was monitored by TLC, was complete after 6 h. The solvents were evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel (heptane to ethyl acetate/heptane, 8:2) to give **5**, which solidified. Recrystallization from a mixture of ether and pentane gave **5** (0.19 g, 79%) as white crystals. Mp: 58−59 °C. ^1H NMR ($CDCl_3$): δ 1.5−1.64 (m, 1 H), 1.88−2.02 (m, 1 H), 1.97 (s, 3 H), 2.07−2.2 (m, 1 H), 2.25−2.39 (m, 1 H), 3.95 (d, J = 7.4 Hz, 1 H), 4.78−4.97 (m, 1 H), 7.11−7.35 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ 19.89, 28.25, 38.84, 57.36, 75.62, 126.18, 128.28, 128.82, 143.44, 175.19. IR (Nujol): $\nu = 1649\ cm^{-1}$. Anal. Calcd for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.62; H, 7.82; N, 5.65.

Direct Kinetic Studies. The method for direct LFP studies has been described.[5] Solutions of **2** in THF were prepared such that the absorbance at 266 nm was 0.8 (1 cm path). The solutions were placed in a jacketed addition funnel and sparged with He. Temperature control was maintained by circulating a solution from a temperature-regulated bath through the jacket of the addition funnel and the well in which the cell was placed. After thermal equilibration, the solutions were allowed to flow thorough a cell. Temperatures were measured with a thermocouple located in the flowing stream above the laser irradiation zone. The samples were irradiated with a 7 ns pulse of 266 nm light from a Nd-YAG laser (ca. 40 mJ), the 335 nm absorbance was monitored, and data were collected on a digital oscilloscope. Each kinetic value in Table 1 was obtained from a summation of 40−50 runs.

Indirect Kinetic Studies. For reactions with *p*-chlorothiophenol, reaction mixtures containing **2** (ca. 0.04 mmol), Bu_3SnH (ca. 0.08 mmol), AIBN (ca. 0.004 mmol), and the desired amount of *p*-chlorothiophenol in 4 mL of cyclohexane/toluene (10:1) were prepared. Reactions were performed under nitrogen. The reactions at 63 and 83 °C were run in a flask equipped with a condenser, and the AIBN was decomposed thermally. At lower temperatures, the reactions were run in flasks contained in a temperature-regulated water bath within the well of a photochemical reactor, and the samples were irradiated with 350 nm light. The reactions were monitored by TLC for disappearance of **2**. After the reactions were complete, the solvent was removed at reduced pressure. The residue was partially purified by chromatography on a short silica gel column with pentane elution (to elute tin-containing compounds) followed by ether elution of the mixture of products. The chromatography procedure completely hydrolyzed imine **6** to the corresponding ketone. A weighed sample of hexadecane was added to the product mixture, and the resulting mixture was analyzed on a GC. Results were

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quantitated with predetermined response factors. The GC yields of **5** plus 6,6-diphenyl-5-hexen-2-one (the ketone from **6**) ranged from 69% to 85%. Repeated chromatographies of one sample showed no apparent change in the ratio of products. Reactions with 1.6 and 3.3 M Bu_3SnH at 83 °C were conducted by this method.

Reactions with thiophenol contained 0.03 mmol of **2**, 11 mg of Bu_3SnH, 5 mg of AIBN, and the appropriate amount of PhSH in 2 mL of cyclohexane. The reactions were conducted as described above. After completion, the solvent was removed at reduced pressure, and the crude product mixture was dissolved in benzene-d_6 and analyzed by ^1H NMR spectroscopy at 300 or 500 MHz. Integrations of the diphenylalkyl proton doublet from **5** (δ 3.86) and the vinyl proton triplet from **6** (δ 5.94) were used to obtain the ratio of products.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for all synthesized compounds (10 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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