

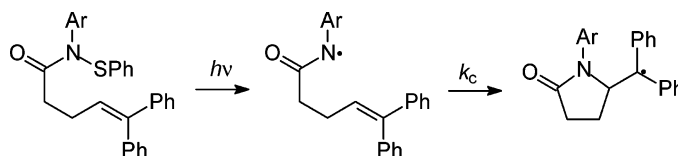
Rate Constants for Anilidyl Radical Cyclization Reactions

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N-Aryl-5,5-diphenyl-4-pentenamidyl radicals (**3**) were produced by 266 nm laser-flash photolysis of the corresponding *N*-(phenylthio) derivatives, and the rate constants for the cyclizations of these radicals were measured directly. The 5-exo cyclization reactions were fast ($k_c > 2 \times 10^5 \text{ s}^{-1}$), and radicals **3** generally behaved as electrophilic reactants with a Hammett correlation of $\rho = 1.9$ for five of the six radicals studied. However, the *p*-methoxyphenyl-substituted radical **3f** cyclized much faster than expected from the Hammett analysis. Variable temperature studies of parent radical **3a** (aryl = phenyl) gave an Arrhenius function with $\log k = 9.2 - 4.4/2.3RT$ (kcal/mol). The rate constant for the reaction of *p*-ethylphenyl-substituted anilidyl radical **3b** with Bu_3SnH at 65 °C was $k_T = 4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

Introduction

Applications of radical reactions for the synthesis of small molecules gained popularity in the past decade largely in the context of carbon-centered radicals.^{1–5} Heteroatom-centered radicals are less common in synthesis, in part because of tedious preparations and instabilities of heteroatom radical precursors. Oxidative entries to heteroatom-centered radicals are attractive because they start from a primary reactant such as an alcohol or amine instead of a derivative. The use of hypervalent iodine reagents for the production of alkoxy radicals from alcohols has developed into an attractive synthetic method.^{6,7}

A number of entries to nitrogen-centered radicals are known,^{8–11} but oxidative entries to these transients have recently

received increased attention. As part of a broad survey of hypervalent iodine reagents in synthesis, Nicolaou and co-workers introduced methodology that involved oxidations of anilides to anilidyl radicals by hypervalent iodine reagents;^{12–17} reactions of several *N*-aryl amides, carbamates, and ureas containing remote unsaturation with *o*-iodoxybenzoic acid (IBX) gave cyclic products, apparently formed via 5-exo radical cyclization reactions. In related works, Studer and Janza reported that IBX oxidation of acylated alkoxyamines gave alkoxyamidyl radicals in good yields,¹⁸ and Suárez and co-workers studied intramolecular hydrogen atom transfer reactions to amidyl radicals produced by reactions of amides with (diacetoxyiodo)-benzene and iodine under irradiation.¹⁹ The generally high yields and the facility of the IBX-promoted anilidyl radical reactions

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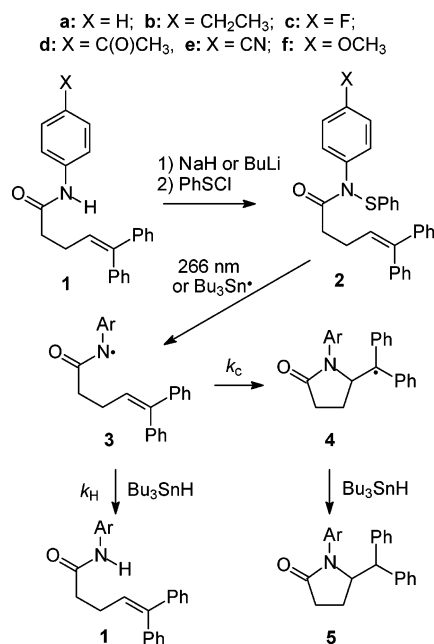
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SCHEME 1



suggest good synthetic utility for this method, but limited kinetic information is available for amidyl radical reactions in general,^{20,21} especially for anilidyl radicals. In this work, we report kinetic results for anilidyl radical reactions that can be used for synthetic planning.

Results and Discussion

We measured rate constants for anilidyl radical cyclization reactions directly via laser flash photolysis (LFP) methods. The design for the kinetic study is illustrated in Scheme 1. Anilides **1** were prepared and converted to the corresponding *N*-(phenylthio)amide derivatives **2** that could serve as radical precursors both for laser flash photolysis (LFP) experiments and chain reactions. Precursors **2b–2f** were prepared by reactions of the corresponding anilides with NaH, and the resulting sodium salts were treated with 1.0 equiv's of PhSCl at 0 °C. This method, which was used previously for preparations of *N*-(phenylthio)amides,²⁰ failed for the preparation of **2a**. We speculate that the sodium salt of anilide **1a** was only slightly soluble in THF and that the PhSCl reagent partially reacted with the alkene moiety. Precursor **2a** was prepared successfully by reaction of the lithium anilide salt, from the reaction of anilide **1a** with BuLi, with PhSCl. The lithium salt method was also used for the preparation of *N*-(phenylthio)acetanilide, which served as a reference compound in the LFP studies.

In the LFP studies, irradiation of precursors **2** with 266 nm light cleaved the N–S bond to give the phenylthiyl radical and the desired anilidyl radicals **3**. Radicals **3** cyclized to give lactam radicals **4** with first-order rate constants k_c . Radicals **4** contain the diphenylalkyl radical moiety, which has a strong chromophore in its UV–visible spectrum, and the kinetics of the cyclization reactions of **3** were measured directly.

In preparative reactions²⁰ with tin hydride present, radical chain reactions were propagated by reactions of the stannyl radical with *N*-(phenylthio)anilides **2** to give radicals **3** that,

TABLE 1. Rate Constants for the Cyclizations of Radicals **3** in THF^a

radical	substituent	σ_p	k_{cyc} (s ⁻¹)	% yield ^b
3a	H	0	$(7.8 \pm 0.3) \times 10^5$	8
3b	CH ₂ CH ₃	-0.13	$(2.5 \pm 0.1) \times 10^5$	13
3c	F	0.15	$(1.3 \pm 0.1) \times 10^6$	46
3d	C(O)CH ₃	0.47	$(3.0 \pm 0.1) \times 10^6$	34
3e	CN	0.70	$(1.4 \pm 0.1) \times 10^7$	34
3f	OCH ₃	-0.12	$(7.7 \pm 0.8) \times 10^7$	82

^a Rate constants determined by laser-flash photolysis in THF at (22 ± 2) °C; errors at 2σ . ^b Isolated percent yields of lactams **5** in nonoptimized preparative reactions.

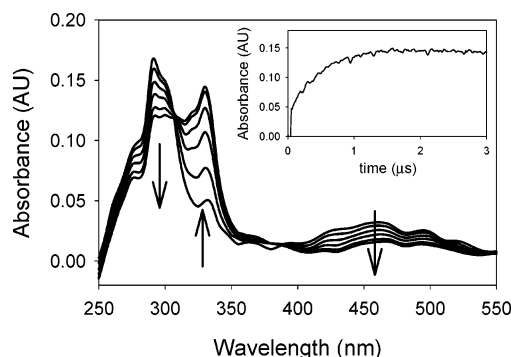


FIGURE 1. Time-resolved spectrum from the reaction of radical **3a** in THF. The time slices are at 0.07, 0.22, 0.47, 0.78, 1.25, and 1.65 μ s. The inset shows the kinetic trace at 335 nm; the decay of product radical **4a** due to radical–radical reactions is apparent by 3 μ s.

again, could cyclize to radicals **4**. Both radicals **3** and radicals **4** react with the tin hydride by hydrogen atom transfer reactions that give acyclic anilides **1** and lactams **5**, respectively. In practice, lactams **5** were isolated from all of the precursors **2** studied in this work. Yields of lactams **5**, which were not optimized, showed an interesting apparent correlation with the cyclization rate constants (Table 1).

Figure 1 shows the results of a typical LFP study with precursor **2a**. The phenylthiyl radical, produced instantly during photolysis, has a strong absorbance with $\lambda_{max} \approx 290$ nm and a broad, weaker absorbance with $\lambda_{max} \approx 450$ nm; signals from this radical are decaying with time in Figure 1. Anilidyl radicals **3** were expected to have no appreciable absorbances at wavelengths greater than 300 nm, and this was confirmed by the production of the acetanilidyl radical from the photolysis of *N*-(thiophenyl)acetanilide. Diphenylalkyl radical **4a** has a long-wavelength absorbance at $\lambda_{max} \approx 335$ nm, and the signal from this radical is growing with time in Figure 1. The inset in Figure 1 shows a kinetic trace at $\lambda = 335$ nm.

Radicals **3** were studied at ambient temperature, and the rate constants determined in LFP studies are listed in Table 1. The reactions were fast, and most of the radicals behaved predictably. Exceptional behavior was observed with *p*-methoxy-substituted radical **3f**, which cyclized quite rapidly. Hammett analysis of the cyclization rate constants is shown in Figure 2. Excluding the results for radical **3f**, the plot gives $\rho = 1.9$, indicating a relatively large increase in negative charge (or decrease in positive charge) at nitrogen in the transition states for the cyclization reactions.

The Hammett study can be compared to that conducted by Nicolaou and co-workers for IBX-promoted anilide cyclizations.¹⁷ In this work, the ρ value was negative, indicating that the positive charge developed on nitrogen during the rate-

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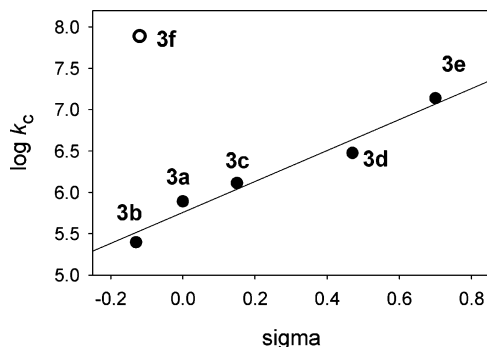


FIGURE 2. Hammett plot for the cyclizations of radicals **3**. Radical **3f** was not included in the regression line.

limiting step in the reaction, and the conclusion was that the electron-transfer reaction between IBX and the anilide (i.e., oxidation of the anilide) was the slow step in the reaction sequence.¹⁷ The demonstration here that the anilidyl radicals display an increase in negative charge on nitrogen in the transition states for cyclization reactions is consistent with previous conclusions; the rate-limiting process in the earlier study¹⁷ could not be the radical cyclization reactions, and oxidations of the anilides were the slow steps in the IBX-promoted reactions.

The cyclization rate constant for radical **3f** was greater than that for any other radical in the series. The value is especially large when the electronic effect of the methoxy substituent is considered, as is apparent in Figure 2 where we used the standard σ value for the *p*-methoxy group. From the Hammett analysis, the expected rate constant for **3f** would be similar to that found for **3b** or more than 2 orders of magnitude smaller than that observed, and the σ^+ value for the methoxy group of -0.87 would predict an even smaller rate constant. The reasonably good correlation for the rate constants for radicals **3a–3e** and the obviously poor fit for radical **3f** suggest that the mechanism for the reaction of radical **3f** is not the same as those for the other radicals **3**. In principle, it is possible that the photolysis reaction of **2f** gave ionic products (i.e., a thiophenoxide anion and an anilide cation),²² but the UV–visible spectrum of the product was that of a diphenylalkyl radical with λ_{\max} at ca. 335 nm and not that of a diphenylalkyl cation, which would have had a very strong signal with λ_{\max} at about 450 nm.^{23,24} The fast reaction of radical **3f** might reflect its behavior as a nucleophilic radical instead of an electrophilic radical as a result of the electron-releasing substituent, but it is possible that the kinetic value for **3f** results from a profoundly different reaction mechanism that we have not envisioned.²⁵

In addition to the large rate constant for the cyclization of radical **3f**, the yield of lactam **5f** in the preparative reaction for

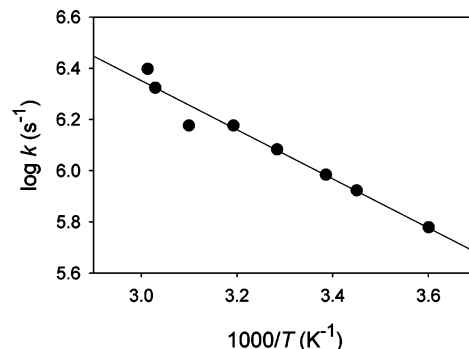
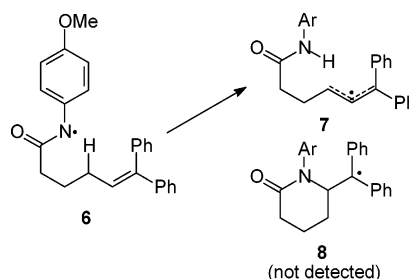


FIGURE 3. Arrhenius plot for the cyclization of radical **3a** in THF.

SCHEME 2



this system was excellent. These interesting observations prompted us to attempt to study the 6-exo cyclization of *p*-methoxy-substituted anilidyl radical **6**. In pairs of analogous radicals that cyclize to give five- and six-membered rings, the 5-exo cyclization typically is about 2 orders of magnitude faster than the 6-exo cyclization.^{26,27} Thus, it appeared possible that 6-exo cyclizations of methoxy-substituted anilidyl radicals might be fast enough for synthetic utility. In practice, however, we did not observe signal growth at 335 nm in the LFP reaction of **6**. Instead, the large signal centered at about 300–305 nm was observed to decay without the apparent formation of any new signal. From previous studies, we expected 1,1-diphenylallyl radical **7** to have a long-wavelength λ_{\max} at ca. 305 nm,²¹ and we speculated that the hydrogen atom transfer of **6** to give **7** would be faster than the cyclization of **6** to give **8** (Scheme 2). For the parent system, that is, anilidyl radical **6** without the phenyl groups on the alkene, the activation energies for 6-exo cyclization and 1,5-H-atom transfer are computed to be similar,²⁸ and efficient 1,5-H-atom transfers in amidyl radicals are well known.^{9,21,29} Given the overlap in absorbance of the phenylthiyl radical with the expected absorbance of **7**, it is possible that **7** was formed with a rate constant smaller than the kinetic limit of our instrument but still remained undetectable.

Variable-temperature studies of the cyclization of radical **3a** in THF were performed between of 5 and 59 °C, and the results are shown in Figure 3. The Arrhenius function for these data is $\log k = (9.2 \pm 0.5) - (4.4 \pm 0.7)/\theta$, where θ is $2.3RT$ in kcal/mol (errors at 2σ). The entropy term, $\log A$, is similar to those found for 5-exo cyclizations of a number of carbon-centered radicals,^{27,30} and we used this $\log A$ value to estimate rate constants for radical **3b** at 65 °C for the tin hydride trapping kinetic studies discussed below.

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(25) A referee of an early draft suggested that the diphenylethene moiety in **3f** might be participating in an internal electron transfer reaction for this radical. Consistent with that conjecture, the relative rate constant for a 5-exo cyclization reaction versus the tin hydride trapping of a *p*-methoxy-substituted anilidyl radical lacking the diphenylethene moiety was smaller than that of the unsubstituted parent.¹⁷ If the rates of the tin hydride trapping of the two radicals are comparable, then the cyclization of the *p*-methoxy-substituted radical in that study was slower than the cyclization of the parent radical, as expected from the results in Figure 2.

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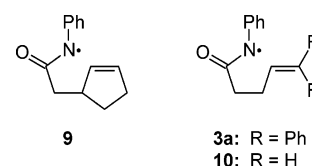
With the cyclization rate constants for anilidyl radicals **3** available, these species can be employed as radical clocks^{31,32} to time competing radical reactions by indirect kinetic studies.²⁶ We applied this method to determine the rate constant for the tin hydride reaction with radical **3b**, which should be useful for synthetic planning purposes. Radical **3b** was the slowest reacting radical in the series we studied, which permitted reasonably efficient tin hydride trapping.

The tin hydride trapping study was conducted at 65 °C. Solutions of radical precursor **2b** and Bu₃SnH in benzene-*d*₆ were equilibrated in a temperature-controlled bath, and the reactions were initiated by the addition of a solution containing AIBN.³³ The reactions required several hours for completion as determined by TLC, which indicates that the chain lengths were quite short. After the reactions were complete, the solutions were concentrated and analyzed by NMR spectroscopy to determine the ratios of acyclic anilide **1b** to lactam **5b**. A plot of [**1b**]/[**5b**] versus tin hydride concentration had a slope of 0.55 ± 0.13 M⁻¹, which is the ratio k_T/k_c , where k_T is the second-order rate constant for the reaction of the radical with Bu₃SnH and k_c is the cyclization rate constant (Scheme 1). To determine k_c for the cyclization of radical **3b** at 65 °C, we estimated the Arrhenius function for this cyclization reaction using the entropic log *A* term for radical **3a** and the observed rate constant for the cyclization of radical **3b** at 22 °C. The approximate Arrhenius function for the cyclization of **3b** thus determined is log *k* = 9.2 - 5.1/2.3RT (kcal/mol), which gives a rate constant for cyclization of **3b** at 65 °C of $k_c = 8 \times 10^5$ s⁻¹.

Assuming a minor solvent effect on the cyclization reaction between benzene and THF,³⁴ the rate constant k_c determined above can be combined with the ratio of rate constants from the competing kinetic study to give a rate constant of $k_T = (4 \pm 1) \times 10^5$ M⁻¹ s⁻¹ at 65 °C for the reaction of radical **3b** with tin hydride. This rate constant is approximately 1 order of magnitude smaller than that for the reaction of tin hydride with a primary alkyl radical at the same temperature.^{35,36} The high reactivity of tin hydride with the relatively stable anilidyl radical is not unexpected because a favorable polarity match exists between the electron-deficient nitrogen radical in **3b** and the electron-rich hydride atom in tin hydride. A similar situation exists with simple amidyl radicals, which react with tin hydride at ambient temperature nearly 3 orders of magnitude faster than do alkyl radicals.^{21,36}

The tin hydride trapping results provide an interesting link with a kinetic result found by Nicolaou and co-workers in their studies of anilidyl radical cyclization reactions. When the cyclization of radical **9** was studied in the presence of Bu₃SnH in toluene at 65 °C, the ratio of rate constants for the trapping

and cyclization of **9** was $k_T/k_c = 0.66$ M.^{14,17} Using the rate constant for the Bu₃SnH reaction with **3b**, we found the estimated rate constant for the cyclization of radical **9** at 65 °C to be $k_c \approx 3 \times 10^5$ s⁻¹. This value is 1 order of magnitude smaller than the rate constant we found for the cyclization of radical **3a** at 65 °C ($k_c = 2 \times 10^6$ s⁻¹). The difference in the kinetics of **9** and **3a** is quite consistent with other radical cyclization rate constants. For example, the diphenyl substitution on the alkene moiety in **3a** is expected to result in radical **3a** cyclizing about 100 times faster than that of hypothetical radical **10** as estimated from the kinetics of many carbon radical pairs,^{27,30} and the ring and alkyl substitution in radical **9** is predicted to result in about a 10-fold acceleration in cyclization in comparison to that for **10**, which is again based on the kinetics of carbon radical pairs.²⁶



Anilidyl- and related aryl-substituted amidyl radicals were shown to be generally useful for synthesis, especially in the context of 5-exo cyclizations, and the oxidative entries to these radicals are very attractive.^{12–17} The rate constants for anilidyl radical reactions found in this work are consistent with previous results and can be used for some aspects of synthetic planning. In terms of reactivities in both cyclization reactions and reactions with tin hydride, anilidyl radicals are 3 to 4 orders of magnitude less reactive than analogous amidyl radicals, a kinetic effect that is somewhat attenuated from that of phenyl group substitution on a carbon-centered radical.^{26,36} In general, 5-exo cyclization reactions of anilidyl radicals are fast enough that interfering radical–radical reactions can be avoided in typical synthetic applications, but attempts at 6-exo cyclizations in analogous anilidyl radicals are expected to be problematic on the basis of our failure to observe a cyclization reaction of radical **6** as well as observations from the synthetic studies by Nicolaou's group.^{12–17} The relatively large effect of the aryl group substituents on the kinetics of the anilidyl radical cyclization reactions is noteworthy and should be considered in synthetic planning.

Experimental Section

Details for the preparation of anilides **1** and the properties of compounds **1**, **2**, and **5** are in Supporting Information.

Sulfenamide Preparation. The following method (method B) was used for the preparation of sulfenamides **2b–2f**. Into a flame-dried, round-bottomed flask equipped with a stirbar, bubbler, and reflux condenser under static nitrogen in a 60 °C water bath was placed 1.0 mmol of anilide **1** and 1.1 equiv of sodium hydride (60% dispersion in oil). To this mixture, 10 mL of THF was added dropwise via a syringe. The mixture was stirred for 40 min or until bubbling ceased. The flask was cooled to -78 °C, and ca. 1.1 equiv of phenylsulfenyl chloride³⁷ was added dropwise (the yellow color of the reagent persisted for approximately 1 min). The mixture was stirred for 10 min and quenched by the addition of 5 mL of saturated aqueous ammonium chloride solution. The crude mixture was diluted with 50 mL of ether, extracted with 1 × 40 mL of saturated sodium bicarbonate solution, 2 × 40 mL of water, and 1 × 40 mL

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(33) Photochemically initiated preparative reactions could be performed, but photochemically initiated kinetic studies were not possible. The phenylthiyl radical formed as a byproduct in the photolysis reaction will react with tin hydride to give highly reactive thiophenol.

(34) Cursory studies showed that a change in solvent from THF to hexane had at most a minor effect on the rate constants for the cyclization of radical **3a**.

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of saturated brine and dried over MgSO_4 . The concentration of the organic layer yielded oils, which were purified by chromatography on silica gel using ethyl acetate/hexanes mixtures to yield *N*-(phenylthio)-amides **2**. Sulfenamide **2a** was prepared by a similar method with the exception of the use of BuLi as the base (Supporting Information).

Preparation of Lactams 5. Solutions of sulfenamide **2** and tri-*n*-butyl tin hydride were prepared as follows. Into a volumetric flask was placed a fixed volume of a stock solution of sulfenamide **2** in THF and a variable amount of distilled Bu_3SnH . The mixture was diluted with the appropriate volume of THF. The solution was transferred to a Spectrosil quartz fluorometer cuvette equipped with a Teflon-coated stirbar and a Teflon-coated screw-cap. Larger preparative reactions were performed in a 3 cm \times 30 cm quartz tube. The solution was degassed with nitrogen for 2 min, capped, and irradiated in a photoreactor using full-spectrum, medium-pressure mercury lamps for 2.0 h. Consumption of the sulfenamide was followed by TLC and was typically completed within 1.5 h. The reaction mixture was transferred to a round-bottomed flask, and the solvent was removed under vacuum. The residue was dissolved in 5 mL of acetonitrile and extracted with 3 \times 5 mL of hexanes to remove excess Bu_3SnH . The acetonitrile was removed under reduced pressure yielding an oily residue, which was dried under high vacuum and then dissolved in acetone- d_6 for NMR analysis. Preparative reactions were then subjected to column chromatography on silica gel using ethyl acetate/hexanes mixtures. Isolated yields of **5**, which were not optimized, are listed in Table 1.

Laser flash photolysis studies were performed as described previously.²⁴ Solutions of **2** in THF were prepared such that the

absorbance at 266 nm was ca. 0.5 AU. Solutions were sparged with helium and allowed to flow through a 1 cm \times 1 cm flow cell. Laser irradiation was accomplished with the fourth harmonic of a Nd:YAG laser (266 nm). All samples showed the growth of a signal with λ_{max} at ca. 335 nm that was reasonably well fit to a first-order exponential function.

Competition Kinetics. A stock solution of **2b** in benzene- d_6 (69 mg/mL) was prepared, and 1.0 mL of this solution was added to three 4-mL glass vials. To these vials was added 0.8, 0.4, and 0.2 mL of Bu_3SnH . The volume in each vial was adjusted to 2.8 mL with benzene- d_6 . The vials were warmed in a bath at 65 $^\circ\text{C}$, and 0.2 mL of a solution containing 25 mg of AIBN in 1 mL of benzene- d_6 was added to each. The final concentrations of Bu_3SnH were 1.0, 0.5, and 0.25 M. After 1.5 h, a second aliquot of AIBN solution (0.2 mL) was added. Consumption of **2b** was monitored by TLC. After **2b** was consumed, the reaction mixtures were cooled to room temperature, concentrated to 1 mL volume under a stream of nitrogen, and analyzed by NMR spectroscopy to determine the ratio of **1b** to **5b**.

Acknowledgment. This work was supported by a grant from the National Science Foundation. E.M. thanks the NIH for fellowship support. We thank an anonymous referee for the mechanistic suggestion noted in ref 25.

Supporting Information Available: Characterization data for compounds **1**, **2**, and **4** and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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