Absolute Kinetics of α-Methoxy Radical Reactions. A Foundation for a Kinetic Scale for α-Alkoxy Radical Reactions

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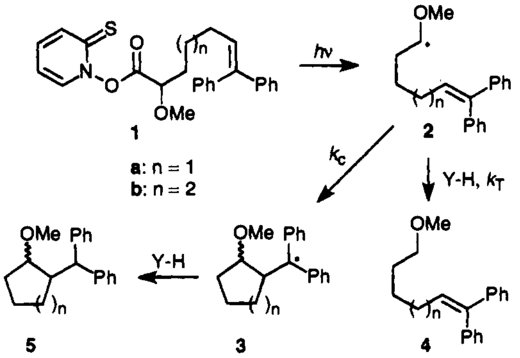
Received January 31, 1994. Revised Manuscript Received September 9, 1994®

Abstract: Rate constants for cyclization of the 1-methoxy-6,6-diphenyl-5-hexenyl radical (**2a**) and the 1-methoxy-7,7-diphenyl-6-heptenyl radical (**2b**) were measured directly. The 5-*exo* cyclization of **2a** in THF and in CH_3CN displays no solvent effect; it is described by $\log(k_c{\cdot}s) = 9.3 - 2.3/2.3RT$, and the rate constant for the cyclization at 25 °C is $3.8 \times 10^7\ s^{-1}$. Radical **2b** cyclizes in a 6-*exo* fashion with rate constants approximately 2 orders of magnitude smaller than those of **2a**; $\log(k_c{\cdot}s) = 8.8 - 4.9/2.3RT$, and k_c at 25 °C is $1.5 \times 10^5\ s^{-1}$. The kinetics of bimolecular hydrogen atom transfer trapping of **2a** by *t*-BuSH ($\log(k_T{\cdot}M{\cdot}s) = 8.4 - 2.1/2.3RT$) and **2b** by Bu_3SnH ($\log(k_T{\cdot}M{\cdot}s) = 8.4 - 3.8/2.3RT$) also were measured. The polarity-matched thiol reacts with **2a** with rate constants similar to those for reaction with a primary alkyl radical, but the polarity-mismatched Bu_3SnH reacts with **2b** about an order of magnitude less rapidly than with an alkyl radical.

An increased knowledge of the kinetics of radical reactions is directly linked to the recent explosive increase in applications of radical-based methods in synthesis and to a better understanding of possible radical intermediates in enzyme-catalyzed reactions. Absolute kinetic scales exist for simple alkyl radicals[1] based on direct measurements of rate constants for reactions of model radicals with Bu_3SnH,[2] PhSH,[3] and 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (TEMPO).[4] However, similar scales are not available for carbon radicals substituted with stabilizing groups. In this paper, we report rate constants for cyclizations of two α-methoxy "radical clocks" [5] measured directly by time-resolved spectroscopic methods. One of the clocking reactions was then used as an indicator for direct measurements of the kinetics of *t*-BuSH reactions with an α-methoxy radical, and the other was used for indirect calibration of the kinetics of Bu_3SnH reactions. These results provide fundamental information necessary for developing an absolute kinetic scale for α-alkoxy radicals that can be used for synthetic planning and in mechanistic studies of biological reactions.

Previous direct kinetic studies of Bu_3SnH and PhSH reactions with simple alkyl radicals employed detection of the radicals produced in bimolecular reactions (i.e., $Bu_3Sn^{\bullet}$ and $PhS^{\bullet}$).[2,3] We have used a different approach (Scheme 1). PTOC ester radical precursors[6] **1** were used as the source of radicals. They are cleaved photochemically by 355 nm light (Nd:YAG laser) to give acyloxyl radicals that rapidly[7] decarboxylate to radicals **2**. Cyclizations of radicals **2** give diphenylalkyl radicals **3** that are readily detected via their strong chromophore with $\lambda_{max} = 328$ nm. Direct measurements of the unimolecular cyclization rate constants (k_c) are made when no competitive bimolecular trapping agents are present. In some cases, bimolecular rate constants (k_T) can be measured directly when radicals **2** are generated in the presence of trapping agents that react with **2** to give acyclic products **4**.[8]

Scheme 1



Results and Discussion

Unimolecular Kinetics. The PTOC precursors **1a** and **1b** were prepared by a conventional sequence from the appropriate carboxylic acids. A radical chain reaction of **1a** conducted in the presence of Bu_3SnH gave products **5a** (formed by 5-*exo* cyclization of the intermediate radical **2a** followed by reaction of the cyclic radicals **3a** with tin hydride) as the only detectable products by ^1H NMR spectroscopy in a 2:1 ratio of *trans* and *cis* isomers. Products **5a** were purified and characterized by NMR spectroscopy and high-resolution MS. PTOC **1b** reacted in the presence of Bu_3SnH to give the products of 6-*exo* cyclization (**5b**, 12:1 mixture of diastereomers) in addition to acyclic product **4b**. The major isomer of **5b** was tentatively identified as *trans* by NMR spectroscopy of the mixture, but compounds **5b** were not completely purified.

® Abstract published in *Advance ACS Abstracts,* February 1, 1995.

(1) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

(2) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739. Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594.

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

(4) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4992 and references therein. See also the discussion in ref 1.

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

(6) PTOC is an acronym for 2-pyridinethione-*N*-oxycarbonyl. See: Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901.

(7) Falvey, D. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 7419. DeCosta, D. P.; Pincock, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 8948.

(8) Formation of **3** is followed spectrophotometrically, but the observed rate constant (k_{obs}) is that for disappearance of radical **2**. That is,

$$k_{obs} = k_0 + k_c + k_T[\text{trap}]$$

where k_c is the rate constant for cyclization, k_T is the second-order rate constant for reaction with trapping agent "trap", and k_0 is a pseudo-first-order rate constant for other reactions (radical–radical reactions, reactions with oxygen) that consume **2**.

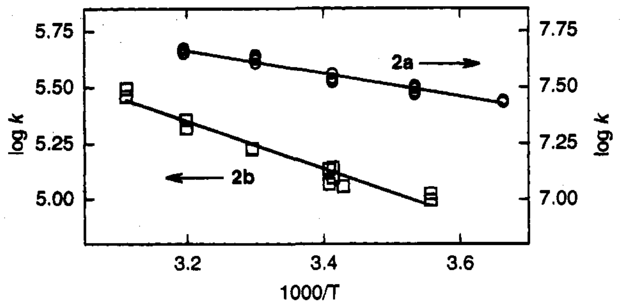


Figure 1. Arrhenius functions for cyclizations of radicals **2a** and **2b** in THF.

The kinetics of the cyclization of radical **2a** were studied over the temperature range 0−40 °C.[9,10] At higher temperatures, the rate of cyclization of **2a** exceeded the dynamic range of our instrument. Each kinetic determination was the average of ca. 15 individual runs, and typical errors in the kinetic determinations were 3% at 2σ. The data for cyclization of **2a** in THF (21 determinations, Figure 1) gave the Arrhenius function in eq 1, and the data for cyclization in CH_3CN (9 determinations) gave the temperature-dependent function in eq 2.[11] The rate constant for cyclization of **2a** at 25 °C is 3.8×10^7 s^{-1}. Despite the presence of the α-methoxy group in **2a**, which is regarded as a stabilizing group on the basis of bond dissociation energy (BDE) values,[12,13] the cyclization rate constants are nearly equal to those for related alkyl radicals lacking the methoxy group.[14,15]

$$\log(k_c\text{·s}) = (9.30 \pm 0.16) - (2.34 \pm 0.22)/2.3RT \quad (\textbf{2a}\text{ in THF}) \quad (1)$$

$$\log(k_c\text{·s}) = (9.23 \pm 0.07) - (2.24 \pm 0.10)/2.3RT \quad (\textbf{2a}\text{ in CH}_3\text{CN}) \quad (2)$$

The lack of a polar solvent effect on the rate constants for cyclization of **2a** is noteworthy. Typically, potential solvent effects are ignored in reactions of simple alkyl radicals,[16] and rate constants for rearrangements of commonly used alkyl radical clocks have been shown via trapping studies to be independent of solvent effects.[17] However, one might have expected a solvent effect in the cyclization of **2a** in which the radical center can be polarized; to the best of our knowledge, this is the first demonstration of the absence of such behavior for a polar radical.

The cyclization of **2b**, from PTOC precursor **1b**, in THF was studied in a similar fashion over the temperature range 10−50 °C. The 6-*exo* cyclization of **2b** is about 2 orders of magnitude less rapid than the 5-*exo* cyclization of **2a**. This leads to an experimental problem for direct kinetic methods in that radical−radical reactions can become a significant part of the total k_{obs},[8] giving artificially large values for the cyclization. In fact, the observed rate constants for reactions of **2b** decreased slightly as the laser power was reduced stepwise from 50 to 4 mJ, as one would expect for a series of measurements with increasingly reduced concentrations of radicals. Therefore, plots of k_{obs} versus laser power were extrapolated to 0 mJ in order to factor the radical−radical reactions out of the observed rate constants. The extrapolated values for k_c gave the Arrhenius function (Figure 1) for cyclization of **2b** in eq 3.[11] As one would expect, the precision of eq 3 is considerably poorer than that of eqs 1 and 2. At 25 °C, the 6-*exo* cyclization of **2b** has a rate constant of 1.5×10^5 s^{-1}. As found for **2a**, the rate constants for the **2b** cyclization reaction are similar to those for the alkyl radical analogs.[18,19]

$$\log(k_c\text{·s}) = (8.76 \pm 0.48) - (4.87 \pm 0.66)/2.3RT \quad (\textbf{2b}\text{ in THF}) \quad (3)$$

Bimolecular Kinetics. In principle, bimolecular rate constants can be determined directly when radicals **2** are produced in the presence of a trapping agent.[8] However, there are limitations to such studies resulting primarily from the use of the PTOC ester precursors. These include (1) a narrow temperature range resulting from the requirement that flowing solutions be employed and from the thermal instability of the precursors, (2) polar reactivity of the PTOC esters (actually mixed anhydrides) with nucleophiles, and (3) a practical requirement that the ratio of the unimolecular to bimolecular rate constants be on the order of 0.1 M. In practice, we were able to determine directly rate constants for reaction of radical **2a** with *t*-BuSH. However, only limited direct kinetic studies of the reaction of **2b** with Bu_3SnH were possible; rate constants for these reactions were determined indirectly by competition studies.[1]

Rate constants for reactions of **2a** in the presence of *t*-BuSH in THF were measured directly at 5, 20, and 35 °C. First-order trapping by the thiol was apparent (Figure 2). The measured rate constants for trapping (k_T) were (4.6 ± 0.7), (5.8 ± 0.9), and 6.7×10^6 M^{-1} s^{-1} at 5, 20, and 35 °C, respectively. Combining the results (18 kinetic determinations) gave the Arrhenius function in eq 4 for reaction of radical **2a** with *t*-BuSH.[11]

$$\log(k_T\text{·M·s}) = (8.4 \pm 0.3) - (2.1 \pm 0.4)/2.3RT \quad (4)$$

The thiol trapping reaction of methoxy-substituted **2a** has rate constants that are indistinguishable from those for reaction of the thiol with a primary alkyl radical, a reaction described by

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[9] PTOC esters (and the related PTOC carbamates) have been employed in direct, laser-based kinetic studies,[10] but their use deserves comment. Because they are readily cleaved with 355 nm light and radical detection is typically at a shorter wavelength, one avoids potential problems from fluorescence in the measurements of fast ($k > 1 \times 10^7$ s^{-1}) reactions.[10b] In addition, the byproduct radical from the PTOC cleavage is the pyridine-2-thiyl radical, which has λ_{max} at 495 nm and little absorbance in the region (310−330 nm) where benzylic and diphenylmethyl radicals absorb strongly.[10] However, the thermal instability[6] of the PTOC esters prevents their use above temperatures of ca. 60 °C.

[10] (a) Bohne, C.; Boch, R.; Scaiano, J. C. *J. Org. Chem.* **1990**, *55*, 5414. (b) Ha, C.; Horner, J. H.; Newcomb, M.; Varick, T. R.; Arnold, B. R.; Lusztyk, J. *J. Org. Chem.* **1993**, *58*, 1194. (c) Newcomb, M.; Horner, J. H.; Shahin, H. *Tetrahedron Lett.* **1993**, *34*, 5523. (d) Newcomb, M.; Horner, J. H.; Filipkowski, M. A.; Ha, C.; Park, S.-U. Submitted for publication.

[11] Activation energies are in kilocalories/mole. All listed errors are 2σ. Higher precision in the Arrhenius functions would be expected if studies were conducted over a wider temperature range.[9] Nevertheless, the precision in the Arrhenius functions for the unimolecular reaction of **2a**, where the observed rate constants were only those of cyclization, is significantly better than the precision typically reported for unimolecular radical reactions. The precision in the function for cyclization of **2b** is comparable to the best values obtained by indirect methods. For the bimolecular reaction of *t*-BuSH with **2a**, the Arrhenius function has about the same precision as the precision reported for other bimolecular hydrogen atom transfer reactions to radicals.[2,3]

[12] The C−H BDE of ethane is 98 kcal/mol, and that of dimethyl ether is 93 kcal/mol.[13]

[13] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493−532.

[14] The rate constants for cyclization of the 6,6-diphenyl-5-hexenyl radical, the 1-methyl-6,6-diphenyl-5-hexenyl radical, and the 1,1-dimethyl-5-hexenyl radical at 20 °C are 3.3, 2.3, and 1.2×10^7 s^{-1}, respectively.[10b,15]

[15] Horner, J. H.; Laksmitpathy, G. Unpublished results.

[16] For a discussion, see ref 1.

[17] Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983.

[18] The rate constants for cyclization of the 7,7-diphenyl-6-heptenyl radical and the 1-methyl-7,7-diphenyl-6-heptenyl radicals at 20 °C are ca. 5 and 2×10^5 s^{-1}, respectively.[19]

[19] Horner, J. H. Unpublished cresults.

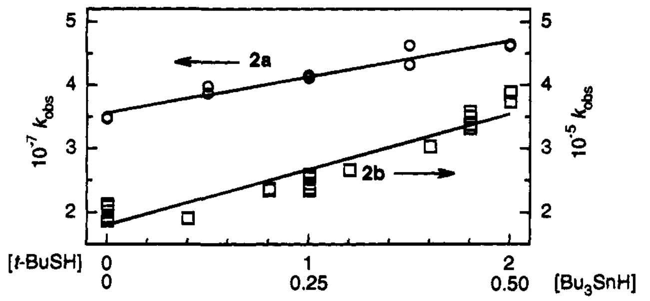

Figure 2. Observed rate constants for reactions of radical **2a** in the presence of *t*-BuSH at 20 °C and radical **2b** in the presence of Bu_3SnH at 25 °C. Note the scale change of the *X* axis for the two reactions.

$\log(k_T\cdot M\cdot s) = 8.4 - 2.0/2.3RT$.[20] In the case of hydrogen atom transfer reactions to radicals, one might expect that the BDE values of the C−H bonds being formed will be related to the activation energies by a free energy function. From this reasoning, the methoxy-substituted radical **2a** should react less rapidly with the thiol than does an alkyl radical because the C−H bond being formed is weaker.[12] However, the "electrophilic" hydrogen atom donor *t*-BuSH is polarity matched with the "nucleophilic" radical **2a**. Therefore, a favorable polarization in the transition state for H-atom transfer is possible, and apparently such an effect offsets a kinetic reduction due to formation of the weaker bond.

The cyclization of radical **2b**, although 2 orders of magnitude less rapid than that of **2a**, was only marginally useful for direct measurements of Bu_3SnH trapping rate constants. At 25 °C, first-order trapping was observed (Figure 2), and we obtained a relatively precise rate constant of $k_T = (3.5 \pm 0.8) \times 10^5$ M^{-1} s^{-1}. This value for reaction of the tin hydride with the secondary α-alkoxy radical **2b** is in good agreement with that reported[21,22] for reaction of a primary α-alkoxy radical with tin hydride, suggesting that it also is accurate. However, the results of direct studies at other temperatures were poorer.[23] Therefore, we employed an indirect kinetic method[1] using **2b** as a classical radical clock.[5]

Reactions of PTOC ester **1b** in the presence of Bu_3SnH were conducted over the temperature range −30 to 66 °C (29 experiments). The yields of cyclic and acyclic products, determined by either GC or 500 MHz ^1H NMR spectral analyses, were combined with the concentrations of Bu_3SnH to give the relative Arrhenius function for trapping and cyclization of **2b** in eq 5. Adding this relative Arrhenius function to that for cyclization of **2b** (eq 3) gave the Arrhenius function for tin hydride trapping in eq 6. The rate constant for tin hydride trapping at 25 °C calculated from eq 6 is 4×10^5 M^{-1} s^{-1}. The excellent agreement between this calculated value and that determined directly (see above) suggests that the kinetic values calculated from eq 6 are more accurate than the precision of the equation indicates.

$$\log[(k_T/k_r)\cdot M] = (-0.4 \pm 0.4) + (1.1 \pm 0.5)/2.3RT \quad (5)$$

$$\log(k_T\cdot M\cdot s) = (8.4 \pm 0.6) - (3.8 \pm 0.9)/2.3RT \quad (6)$$

Again, it is instructive to compare the kinetics of reactions of the hydrogen atom donor with the methoxy-substituted radical and unsubstituted alkyl radicals. Alkyl radicals react with tin hydride with rate constants of about 2×10^6 M^{-1} s^{-1} at 25 °C,[2] nearly an order of magnitude faster than does radical **2b**. As noted above, the reduced BDE value for an α-methoxy C−H bond in comparison to an alkyl C−H bond should be reflected in a diminished rate constant for H-atom transfer to the former radical from a common agent. In the case of tin hydride reacting with the methoxy-substituted radical, both species are electron rich, and a favorable polarization in the transition state is less likely than in the case of the thiol reaction.

The kinetic values obtained in this work can be employed in the construction of a kinetic scale for α-methoxy radical reactions. The clocks can be used for timing various bimolecular trapping reactions. Because the rate constants for radical reactions are little influenced by solvent effects, one can employ the rate constants for *t*-BuSH and Bu_3SnH trapping in synthetic planning.[24] Both the unimolecular and bimolecular kinetics should be useful in calculations of radical reaction transition states.[25] The rate constants for reactions of the simple thiol with **2a** might serve as useful first approximations for the rate constants for reactions of cysteine residues in proteins with neutral sugar radicals.[26]

Experimental Section

1-[[(1-Methoxy-6,6-diphenyl-5-hexenyl)carbonyl]oxy]-2(1*H*)-pyridinethione (1a).[27] Treatment of 2-methoxy-7,7-diphenyl-6-heptenoic acid with oxalyl chloride followed by treatment with the 2-mercaptopyridine *N*-oxide sodium salt by the previously reported method[6] gave compound **1a** in 66% yield as a light yellow oil that was >95% pure by ^1H NMR analysis. ^1H NMR ($CDCl_3$): δ 1.66–1.75 (m, 2 H), 1.85–2.10 (m, 2 H), 2.19 (q, *J* = 8 Hz, 2 H), 3.58 (s, 3 H), 4.14 (m, 1 H), 6.08 (t, *J* = 7 Hz, 1 H), 6.67 (t, *J* = 6 Hz, 1 H), 7.10–7.45 (m, 11 H), 7.56 (d, *J* = 7 Hz, 1 H), 7.70 (d, *J* = 8 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 25.3, 29.2, 32.2, 58.5, 79.1, 111.1, 113.5, 126.9, 127.1, 128.0, 128.2, 128.8, 129.8, 132.8, 137.1, 137.6, 140.0, 141.2, 142.5.

1-[[(7,7-Diphenyl-1-methoxy-6-heptenyl)carbonyl]oxy]-2(1*H*)-pyridinethione (1b)[27] was prepared as above from 2-methoxy-8,8-diphenyl-7-octenoic acid. Compound **1b** was obtained in 66% yield after chromatography as a bright yellow oil that was >95% pure by ^1H NMR analysis. ^1H NMR ($CDCl_3$): δ 1.52 (m, 4 H), 1.90 (m, 1 H), 1.96 (m, 1 H), 2.16 (q, *J* = 6.9 Hz, 2 H), 3.56 (s, 3 H), 4.17 (dd, *J* = 7.8, 4.3 Hz, 1 H), 6.09 (t, *J* = 7.5 Hz, 1 H), 6.61 (dt, *J* = 6.9, 1.9 Hz, 1 H), 7.31–7.15 (m, 9 H), 7.36 (m, 2 H), 7.53 (d, *J* = 6.8 Hz, 1 H), 7.68 (d, *J* = 8.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 24.7, 29.4, 32.6, 59.2, 79.7, 113.6, 126.8, 126.9, 127.2, 128.1, 128.2, 129.5, 129.9, 132.9, 137.1, 137.6, 140.1, 141.9, 142.6, 170.6.

Reaction of 1a with Bu_3SnH. A solution of 168 mg (0.4 mmol) of **1a** and 0.54 mL (2.0 mmol) of Bu_3SnH in 20 mL of THF was irradiated overnight with a 150 W tungsten filament lamp. Solvent was distilled *in vacuo*, and the residue was dissolved in benzene. A solution of I_2 in CH_2Cl_2 was added dropwise with stirring until a red color persisted. The solution was washed with aqueous saturated KF solution, and the organic phase was filtered to remove precipitate. The

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[20] Newcomb, M.; Glenn, A. G.; Manek, M. B. *J. Org. Chem.* **1989**, *54*, 4603.

[21] Beckwith and Glover[22] employed kinetic ESR spectroscopy to determine $\log(k_T\cdot M\cdot s) = 9.1 - 5.0/2.3RT$ ($k_T = 3 \times 10^5$ M^{-1} s^{-1} at 25 °C) for reactions of the 2-oxa-5-hexenyl radical with Bu_3SnH.

[22] Beckwith, A. L. J.; Glover, S. A. *Aust. J. Chem.* **1987**, *40*, 157–173.

[23] Because $k_r/k_T \approx 1$ M, high concentrations of Bu_3SnH were required. Apparently, viscous concentrated solutions of Bu_3SnH mixed poorly with solutions of **1b**. Incorporation of a porous metal baffle after the mixing tee did not improve the results.

[24] For leading references to synthetic methods employing α-alkoxy radicals, see: Curran, D. P.; Shen, W. *J. Am. Chem. Soc.* **1993**, *115*, 6051. Kock, A.; Lamberth, C.; Wetterich, F.; Giese, B. *J. Org. Chem.* **1993**, *58*, 1083. Rawal, V. H.; Singh, S. P.; Dufour, C.; Michoud, C. *J. Org. Chem.* **1993**, *58*, 7718.

[25] For recent high-level *ab initio* calculations of α-alkoxyl radicals, see: Lee, M.-S.; Jackson, J. E. Submitted for publication. We thank Prof. Jackson for informing us of these results prior to publication.

[26] For leading references to radical reactions of sugars in nucleic acids, see: Stubbe, J.; Kozarich, J. W. *Chem. Rev.* **1987**, *87*, 1107. Reichard, P. *Annu. Rev. Biochem.* **1988**, *57*, 349. Stubbe, J. *Ann. Rev. Biochem.* **1989**, *58*, 257. Nicolaou, K. C.; Dai, W.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387. Reichard, P. *Science* **1993**, *260*, 1773. Giese, B.; Burger, J.; Kang, T. W.; Kesselheim, C.; Wittmer, T. *J. Am. Chem. Soc.* **1992**, *114*, 7322.

[27] Detailed experimental procedures for the preparations of **1a** and **2a** are given in the supplementary material.

solution was washed again with the KF solution and then extracted with 5% aqueous $Na_2S_2O_4$ solution. Concentration of the solution *in vacuo* gave 240 mg of residue. An ^{1}H NMR spectrum of the crude product revealed the presence of two diastereomers of **5a** in a 2:1 ratio and tin-containing compounds. Column chromatography (silica gel, pentane—ether, 95:5, v/v) effected separation of **5a** from the tin-containing compounds and partial separation of the **5a** diastereomers. Radial chromatography (2 mm silica gel plate, pentane—ether, 95:5, v/v) of the partially purified diastereomers gave samples of each which were free of contamination by the other. The major diastereomer was assigned as *trans*-**5a**, and the minor as *cis*-**5a** on the basis of the coupling constants for the C1 and C2 protons of 4 and 2 Hz, respectively.

***trans*-2-(Diphenylmethyl)-1-methoxycyclopentane (*trans*-5a):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.3—1.5 (m, 1 H), 1.5—1.7 (m, 4 H), 1.7—1.9 (m, 1 H), 2.58 (dddd, J = 11.5, 11.5, 7.5, 4.0 Hz, 1 H), 3.04 (s, 3 H), 3.30 (broad t, J = 4 Hz, 1 H), 4.11 (d, J = 11 Hz, 1 H), 7.1—7.4 (m, 10 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.1, 28.6, 29.7, 50.5, 51.7, 56.1, 82.8, 125.8, 125.9, 128.0, 128.2, 128.3, 129.2, 144.4, 144.7. MS: *m/z* (relative intensity) 266 (M^+, 10), 235 (19), 234 (97), 168 (20), 167 (100), 165 (24). HRMS: calcd for $C_{19}H_{22}O$, 266.1670; found, 266.1664.

***cis*-2-(Diphenylmethyl)-1-methoxycyclopentane (*cis*-5a):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.0—1.3 (m, 1 H), 1.6—1.8 (m, 4 H), 1.7—1.9 (m, 1 H), 2.75—2.95 (mutiplet with one doublet with J = 2 Hz, 1 H), 2.99 (s, 3 H), 3.39 (dt, J = 5, 2 Hz, 1 H), 3.56 (d, J = 12 Hz, 1 H), 7.1—7.4 (m, 10 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.2, 30.2, 31.0, 49.6, 56.1, 56.2, 77.4, 86.2, 94.8, 126.1, 128.2, 128.3, 128.4, 144.4, 144.6, 179.1. MS: *m/z* (relative intensity) 266 (M^+, 2), 234 (11), 168 (81), 167 (100), 165 (20), 99 (21). HRMS: calcd for $C_{19}H_{22}O$, 266.1670; found, 266.1664.

Reaction of 1b with Bu_3SnH. A degassed solution of PTOC ester **1b** (83 mg, 0.14 mmol) and Bu_3SnH (0.81 mL, 3.0 mmol) in 3 mL of dry benzene was irradiated for 2 h with a 250 W tungsten filament lamp. Solvent removal and chromatography (silica gel, hexanes—ethyl acetate, gradient of 100:0 to 1:1, v/v) gave a mixture of acycle **4b** and the two cyclic diastereomers of **5b** in 43% yield in a ratio of ca. 36:12:1 as determined by GC (15 m, SE-30, wide-bore capillary column, Alltech). The order of GC elution was minor isomer of **5b**, major isomer of **5b**, **4b**. The major product was identified as **4b** by comparison of its NMR spectrum, GC retention time, and mass spectral fragmentation pattern to those of an authentic sample prepared by methylation of the corresponding alcohol. Cyclic products **5b** were partially characterized by analysis of the ^{1}H NMR spectrum of the major isomer (as deduced from the spectrum of the mixture of products) and the mass spectral fragmentation patterns. The major diastereomer of **5b** was tentatively identified as *trans*-**5b** on the basis of a ca. 8 Hz coupling constant between the protons on C1 and C2.

***trans*-2-(Diphenylmethyl)-1-methoxycyclohexane (*trans*-5b):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.3—1.6 (m, 8 H), 2.5 (qd, J = 3.7, 8.0 Hz, 1 H), 2.86 (td, J = 3.3, 7.4 Hz, 1 H), 3.23 (s, 3 H), 3.38 (d, J = 7.9 Hz, 1 H), 7.15—7.4 (m, 10 H). MS: *m/z* (relative intensity) 280 (3), 248 (82), 205 (16), 180 (16), 167 (100), 152 (16), 113 (18), 81 (35).

Kinetic Methods. The direct method was the same as that previously reported.[10b,c] An Applied Photophysics LK-50 kinetic spectrometer employing a Spectron Nd:YAG laser was used. Studies were conducted with solutions of **1** that were flowing through a cell in a temperature-regulated well. For studies in the absence of a trapping agent, solutions were thermally equilibrated in a jacketed addition funnel with continual He sparging. For studies in the presence of a trapping agent, He-sparged solutions of **1** and the trapping agent were placed in 50 mL gas-tight syringes, and the solutions were pumped via a syringe pump through stainless steel coils contained in a temperature-regulated bath. The solutions were mixed for <5 s before entering the flow cell. Temperatures of the flowing solutions were measured with a thermocouple placed after the irradiation zone of the flow cell.

The indirect method was conventional.[1] Solutions of PTOC ester **1b** and Bu_3SnH in THF in a shielded flask were equilibrated at the desired temperature before being irradiated. For reactions at 44 and 66 °C, the solutions were treated with iodine, washed with aqueous KF and NaCl solutions, dried ($MgSO_4$), and analyzed by GC. For reactions at −30, 0, and 25 °C, the solvent was removed *in vacuo*, the resulting residue was dissolved in benzene-d_6, and the solution was analyzed by 500 MHz ^{1}H NMR spectroscopy.

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE-9117929) and the National Institutes of Health (GM-48722).

Supplementary Material Available: Detailed experimental procedures for the preparation of PTOC esters **1a** and **1b** (5 pages). This material is contained in many 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.

JA940315C