been absolutely ruled out. In fact, on the basis of molecular dynamic simulations, plus structural and stereoelectronic considerations, Karplus has recently suggested mechanism (b) to be a more favorable pathway for lysozyme action.[5]

Since either path (a) or (b) eventually yields the same solvolysis product **4** when alcohol or water is the trapping nucleophile, product studies have not been useful in distinguishing between (a) and (b).[10] An unambiguous way to differentiate between routes (a) and (b) would be to trap the intermediate oxocarbonium ion(s) so as to obtain distinguishable product(s). We report herein the results of trapping experiments which clearly demonstrate that both pathways (a) and (b) are operative in the proton-catalyzed cleavage of alkyl β-THP acetals.

Our trapping method is a C–C bond-forming reaction via intramolecular attack of an enamine on an oxocarbonium ion generated in situ from acid-catalyzed cleavage of an acetal.[11] When our starting acetal **5**, which has two trans diequatorial groups on the THP ring, was stirred with Dowex-50 X 8-H^+ and anhydrous methanol for about 3 days at room temperature, a mixture of three compounds **6**, **7**, and **8** was obtained (Table I; entry 1).

The formation of major products **6** and **7** is easily rationalized by assuming the intermediacy of oxocarbonium ions **9** and **10** formed as a result of exocyclic C–O bond and endocyclic C–O bond cleavages, respectively (Scheme II). Transformations[11] subsequent to the ring closure step in each case then lead to structures **6** and **7**. The formation of minor product **8**, however, cannot be straightforward. The precursor to **8** must be the oxocarbonium ion **11** which could result either from the rotation of oxocarbonium ion **10** around the C–C bond or, alternatively, from the cleavage of acetals **12** and **13a** formed as a result of competitive solvent (methanol) trapping of the oxocarbonium ions **9** and **10**, respectively.[12,13] To test these possibilities compound **14**, the ethyl acetal analogue of **5**, was stirred with Dowex-H^+ and methanol, and four products **6**, **7**, **8**, and **15** were isolated (Table I; entry 2).[14] The absence of product **16** (which could only arise via rotation of the initially formed intermediate oxocarbonium ion **17** followed by ring closure) and the presence of **7** and **8** provide support for the solvent attack mechanism for formation of the minor products.

We also treated THP acetals **18** and **19**, which have all equatorial substituents, with Dowex-H^+ and methanol. The results are summarized in Table I (entries 3 and 4) and are consistent with those obtained in the cases of **5** and **14**.

In summary, we have provided concrete experimental evidence which demonstrates that in proton-catalyzed solvolysis there is the possibility for both exo- and endocyclic C–O bond cleavages of THP acetals.[15] We believe that our findings require a fresh look at the early conclusions favoring exclusive exocyclic C–O bond cleavage of THP acetals[8c,d,h] and at subsequent interpretations based on the early precedent.[7a,f,16] In addition, our method will be important for the examination of the role of stereoelectronic effects in acetal hydrolysis.[1b-d,3c,h,l,m]

Acknowledgment. We are indebted to the National Cancer Institute for Grant CA-39351, to the American Cancer Society for grant CH-272, and to CUNY for PSC research awards which supported this work. The NMR spectrometers used in the research were purchased with funds awarded by NSF-PCM-111745 and NIH-RR-03214.

(9) While our manuscript was in the review process, Guindon reported that dimethylboron bromide in CH_2Cl_2 served to cleave the endocyclic C–O bond in THP acetals and glycosides. (a) Guindon, Y.; Bernstein, M. A.; Anderson, P. C. *Tetrahedron Lett.* **1987**, *28*, 2225. (b) Guindon, Y.; Anderson, P. C. *Ibid.* **1987**, *28*, 2485.

(10) A similar question regarding exo- versus endocyclic carbon–heteroatom bond cleavage arises in the hydrolysis of cyclic ortho esters and related systems. However, due to the formation of different products, the identification of the position of bond cleavage is not ambiguous. (a) For a review see: ref 1d, Chapter 3. (b) For a recent article, see: Khouri, F. F.; Kaloustian, M. K. *J. Am. Chem. Soc.* **1986**, *108*, 6683 and references therein.

(11) Gupta, R. B.; Franck, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 5393.

(12) Intramolecular trapping of the oxocarbonium ion **10** by the hydroxyl group may also generate **12**.

(13) We have already observed that the rotation of oxocarbonium ions around the C–C bond in these systems is slow compared to solvent trapping and is almost nonexistent.[11] Also, the formation of acetals **12** and **13** as a result of competing solvent trapping of the oxocarbonium ions is reminescent of the initial formation of **5**.

(14) The increase in the formation of products resulting from the ring-opening mechanism of acetal in the case of **14** as compared to **5** (Table I; entries 1 and 2) is consistent with our earlier observation in these systems that ethanol is a poorer leaving group than methanol.[11]

(15) As a referee states, the observed percentage of endocyclic cleavage is only the minimum since there is no measure for the fraction of reclosure of intermediate, e.g., **10** to starting THP acetal **5**.

(16) Beaulieu, N.; Dickinson, R. A.; Deslongchamps, P. *Can. J. Chem.* **1980**, *58*, 2531.

1,3-Asymmetric Induction in Intramolecular Reformatsky-Type Reactions Promoted by Samarium Diiodide†[1]

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Extraordinary strides have been made in recent years in development of synthetic methods which permit stereochemical control in construction of acyclic organic molecules.[3] Perhaps most dramatic have been those conceptual advances which permit 1,3-relative asymmetric induction by carbon–carbon bond-forming reactions utilizing β-heterosubstituted carbonyl substrates.[4] Still, truly general methods for such processes have yet to emerge. For example, few reported methods of 1,3-asymmetric induction provide more than 10:1 diastereoselectivity for representative substrates.[4d-f,j] Many such processes appear to be useful for β-alkoxy aldehydes but not corresponding ketones or vice versa.[4] Finally, no studies of which we are aware have addressed the important problem of 1,3-asymmetric induction in substrates where substituents α to the carbonyl may affect the stereochemical outcome in reactions of interest.

Inherent geometrical constraints imposed by intramolecular carbonyl addition reactions provide an attractive means by which to achieve 1,3-relative asymmetric induction, and this approach has been effectively employed by several research groups.[4d,g-j] Intramolecular Reformatsky reactions of bromoacetates derived from β-hydroxy carbonyl substrates provide a very promising variant of the intramolecular carbonyl addition approach to 1,3-asymmetric induction. However, only limited success has been realized along thse lines with zinc-promoted reactions, as low yields and/or poor diastereoselectivities have been observed in studies reported to date.[5] Our success in utilizing samarium diiodide

† Dedicated to Professor Herbert C. Brown on the occasion of his 75th birthday.

(1) Lanthanides in Organic Synthesis. 8.

(2) Alfred P. Sloan Research Fellow, 1987–1989.

(3) (a) Bartlett, P. A. *Tetrahedron* **1979**, *36*, 2. (b) Eliel, E. L. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1983; Vol. 2.

(4) (a) Leitereg, T. J.; Cram, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 4019. (b) Michel, J.; Canonne, P. *Can. J. Chem.* **1971**, *49*, 4084. (c) Fouquey, C.; Jacques, J.; Angliolini, L.; Tramontini, M. *Tetrahedron* **1974**, *30*, 2801. (d) Reetz, M. T.; Jung, A. *J. Am. Chem. Soc.* **1983**, *105*, 4833. (e) Heathcock, C. H.; Kiyooka, S.; Blumenkopf, T. A. *J. Org. Chem.* **1984**, *49*, 4214. (f) Reetz, M. T.; Kesseler, K.; Jung, A. *Tetrahedron Lett.* **1984**, *25*, 729. (g) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 556. (h) Hoffmann, R. W.; Froech, S. *Tetrahedron Lett.* **1985**, *26*, 1643. (i) Reetz, M. T. *Pure Appl. Chem.* **1985**, *57*, 1781. (j) Ikeda, N.; Omori, K.; Yamamoto, H. *Tetrahedron Lett.* **1986**, *27*, 1175.

(5) (a) Fuson, R. C.; Thomas, N. *J. Org. Chem.* **1953**, *18*, 1762. (b) Hulchen, F. H.; Hosick, T. A. *Chem. Abstr.* **1964**, *60*, 10554g. (c) Gaudemar, M. *Organomet. Chem. Rev. A* **1972**, *8*, 183. (d) Rathke, M. W. *Org. React.* **1975**, *22*, 423. (e) Sato, A.; Ogiso, A.; Noguchi, H; Mitsui, S.; Kaneko, I.; Shimada, Y. *Chem. Pharm. Bull.* **1980**, *28*, 1509. (f) Stokker, G. E.; Hoffman, W. F.; Alberts, R. W.; Cragoe, E. J., Jr.; Deana, A. A.; Gilfillan, J. L.; Huff, J. W.; Novello, F. C.; Prugh, J. D.; Smith, R. L.; Willard, A. K. *J. Med. Chem.* **1985**, *28*, 347.

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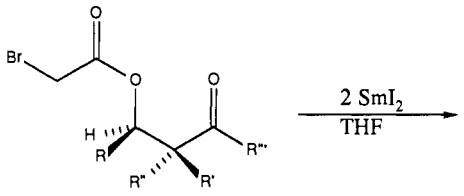
Table I. 1,3-Asymmetric Induction via Samarium Diiodide Promoted Intramolecular Reformatsky Reactions[a]

entry	substrate	R	R′	R″	R‴	% isoltd yield **2**
1	**1a**	Ph	H	H	Me	95[b]
2	**1b**	Ph	H	H	*t*-Bu	98[b]
3	**1c**	*n*-Pr	H	H	H	69[b]
4	**1d**	H	H	Me	*t*-Bu	85[c]
5	**1e**	Ph	H	Me	*t*-Bu	71[c]
6	**1f**	*n*-Pr	H	Me	Et	86[b]
7	**1g**	*n*-Pr	Me	H	Et	97[d] (65[b,e])
8	**1h**	Ph	H	Me	H	65[f]
9	**1i**	Ph	Me	H	H	62[f]

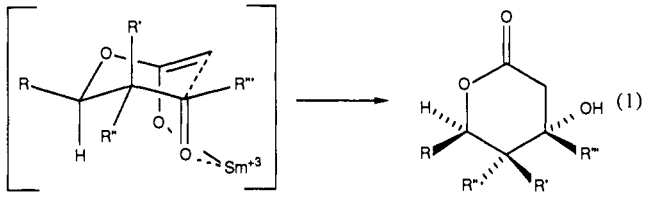
[a] Substrates were added to 2 equiv of SmI_2 in THF at the indicated temperatures. All reactions were complete in less than 15 min. [b] Reaction performed at −78 °C. [c] Reaction performed at 0 °C. [d] Reaction performed at −20 °C. An 8:1 mixture of diastereomers was generated. [e] A 13:1 mixture of diastereomers was generated. [f] Reaction performed at ambient temperature.

(SmI_2) as a soluble reagent for stereocontrolled intramolecular Barbier-type syntheses[6] prompted us to explore use of this reagent for generation of acyclic syn 1,3-diol equivalents via an intramolecular Reformatsky-type reaction.[7]

We envisioned that treatment of β-bromoacetoxy carbonyl substrates **1** with SmI_2 would initially generate Sm^{3+} ester enolates. Cyclization was expected to ensue through a rigid cyclic transition state enforced by chelation, providing the desired β-hydroxy δ-valerolactones **2** (eq 1) of defined stereochemistry. Indeed, this process works extraordinarily well, and we are pleased to report our results outlining what we believe is a most general and effective method for 1,3-asymmetric induction by a carbon–carbon bond-forming process.



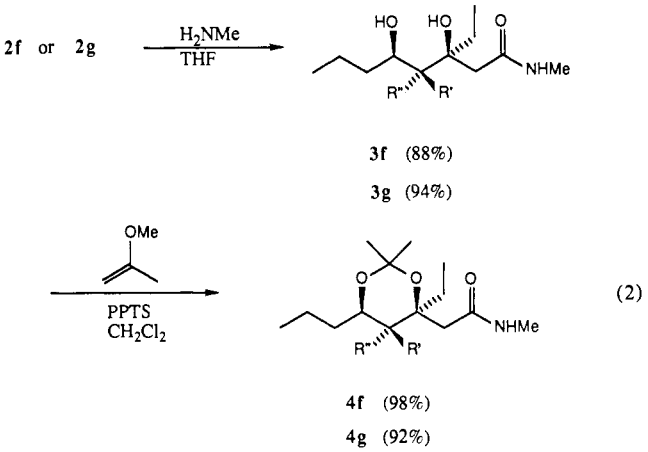
1



(1)

2

As depicted in Table I, the reaction is amazingly broad in scope. Crude reaction mixtures were analyzed by capillary gas chromatography on a fused silica capillary column, and, with one exception (entry 7, vide infra), a single diastereomer is generated in all cases. The sense of 1,3-asymmetric induction is consistent with that predicted by the empirical model for all of these examples. Stereochemistry was assigned on the basis of spectral data for known compounds (entry 3), X-ray crystal structure determinations of the products (entries 1, 2, 4, 5, 8, 9), or X-ray crystal structure determinations of acetonide derivatives generated from the products (eq 2 for entries 6 and 7).



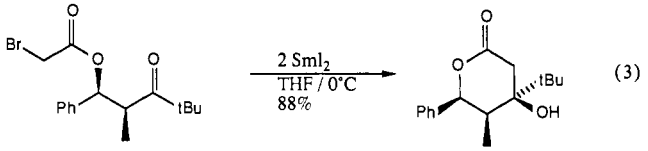
(2)

4f (98%)

4g (92%)

In contrast to previously reported methods of 1,3-asymmetric induction, aldehydes (entries 3, 8, and 9) as well as ketones are suitable substrates for the reaction. Perhaps most importantly, strict 1,3-relative asymmetric induction was observed in these examples, *even in diastereomeric pairs of substrates bearing α substituents*. Thus, although the diastereoselectivity is somewhat attenuated for the syn diastereomer where the α substituent would be axially disposed in the proposed transition structure leading to product (substrate **1g**, entry 7), 1,3-asymmetric induction is still predominant and overpowers any other factors to an impressive extent.

We have found a single exception thus far to this general reactivity pattern (eq 3). In this system, a single diastereomer is detected and can be isolated in excellent yield. An X-ray crystal



(3)

structure determination of the product, however, indicates that the sense of relative 1,3-asymmetric induction is opposite to that observed in all other examples. Steric factors may preclude access to the chelated chair transition structure depicted in eq 1 for this substrate. Thus, Ph-Me and *t*-Bu-Me butane gauche interactions as well as unfavorable steric interactions between the axial methyl group and the *t*-Bu methyl groups that would be encountered in the chelated chair may provide an overwhelming impediment to accessing such a conformation, thereby forcing another transition structure to predominate in this instance. Studies designed to further elucidate the precise factors involved in this dramatic switch in the sense of 1,3-asymmetric induction and to more extensively outline the scope of the reaction with perhaps more demanding substrates are currently underway.

In conclusion, it should be noted that no protecting groups are required in this process since the alcohol "protecting group" becomes the reacting nucleophile for the reaction. As a consequence, for most substrates of interest the SmI_2-promoted intramolecular Reformatsky reaction provides the most efficient method yet developed for generation of acyclic syn 1,3-diol equivalents via carbon–carbon bond-forming reactions. Furthermore, the method provides perhaps the most effective entry into stereodefined β-hydroxy δ-valerolactones **2**.[5e,f] Molecules possessing this functional array, structurally analogous to compactin lactone, are potent inhibitors of HMG-CoA reductase, the key enzyme involved in biosynthesis of cholesterol.[5e,f,8] The successful development of this methodology thus provides facile entry into a variety of im-

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portant stereodefined acyclic molecules as well as an improved route to biologically active β-hydroxy δ-valerolactones heretofore difficult to access by more traditional means.

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Supplementary Material Available: General synthetic procedure and complete spectral data for all compounds synthesized as well as X-ray crystal structure data (25 pages). Ordering information is given on any current masthead page.

Atom Transfer Cycloaddition. A Facile Preparation of Functionalized (Methylene)cyclopentanes

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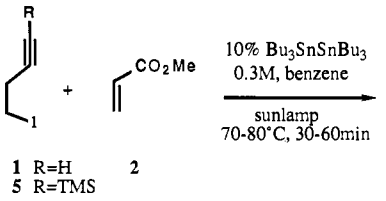
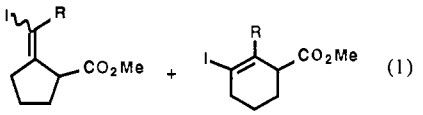
The ability to sequence radical reactions to accomplish multiple transformations in a single step is an asset of free radical reactions in organic synthesis.[2,3] In designing such sequences, it is advantageous to permit long lifetimes for intermediate radicals so that desired reactions can occur. On the other hand, the chain-transfer step should be as rapid as possible to prevent diversion of the final radical along undesired pathways. While a variety of useful radical sequences have recently been developed, the methods available to conduct these free radical reactions are actually quite few. The most commonly employed method uses a tin hydride reagent to mediate the radical sequence.[4,5] In the tin hydride method, radical substituents have little effect on the rate of hydrogen atom abstraction, and, to a first approximation, most radicals have similar lifetimes with respect to H-atom abstraction.[6] This can be a serious problem, particularly in the design of sequences containing a relatively slow intermediate step. While free-radical reactions based on halogen atom transfer have long been known,[7,8] the unique capability of such "atom transfer based"[9,10] methods to control the course of sequential free radical reactions has not been recognized. We now report the sequencing of a free radical addition and cyclization reaction which is uniquely controlled by iodine atom transfer. This simple method for the preparation of (iodomethylene)cyclopentanes is termed "atom transfer cycloaddition".[9]

Sunlamp irradiation for 30 min of a solution of butynyl iodide (**1**) (0.3 M) and methyl acrylate (0.3 M) in benzene (~80 °C) containing 10 mol % hexabutylditin produced a mixture of (iodomethylene)cyclopentane **3** and cyclohexenyl iodide **4**.[11] The



1 R=H
5 R=TMS



(1)

3 (3/1 E/Z) 15/1 **4**
6 **7**

ratio of **3**/**4** was 15:1, and (iodomethylene)cyclopentane **3** was a 3:1 mixture of stereoisomers with the *E*-isomer predominating.[12]

(1) Sloan Foundation Fellow, 1985-87; Dreyfus Teacher-Scholar, 1985-89; Eli Lilly Grantee, 1985-87; Merck Faculty Development Awardee, 1986-87; Recipient of a National Institutes of Health Career Development Award, 1987-92.

(2) Examples of sequential radical reactions include the following (a) Beckwith, A. L. J.; Phillipou, G.; Serelis, A. K. *Tetrahedron Lett.* **1981**, *22*, 2811. (b) Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386. (c) Julia, M. *Pure Appl. Chem.* **1974**, *40*, 553. (d) Breslow, R.; Olin, S. S.; Groves, J. T. *Tetrahedron Lett.* **1968**, 1837. (e) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1726. (f) Chatzopoulos, M.; Montheard, J.-P. *C. R. Hebd. Seances Acad. Sci. Ser. C* **1975**, *280*, 29. (g) Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 3720. (h) Stork, G.; Mook, R., Jr.; Biller, S. A.; Rychnovsky, S. D. *Ibid.* **1983**, *105*, 3741. (i) Stork, G.; Sher, P. M. *Ibid.* **1983**, *105*, 6765. (j) Stella, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 337. (k) Moriya, O.; Kakihana, M.; Urata, Y.; Sugizaki, T.; Kageyama, T.; Ueno, Y.; Endo, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1401. (l) Feldman, K. S.; Simpson, R. E.; Parvez, M. *J. Am. Chem. Soc.* **1986**, *108*, 1328. (m) Beckwith, A. L. J.; Roberts, D. H.; Schiesser, C. H.; Wallner, A. *Tetrahedron Lett.* **1985**, *26*, 3349. (n) Winkler, J. D.; Sridar, V. *J. Am. Chem. Soc.* **1986**, *108*, 1708. (o) Tsang, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1986**, *108*, 2216. (p) Stork, G.; Sher, P. M.; Chen, H. L. *J. Am. Chem. Soc.* **1986**, *108*, 6384. (q) Curran, D. P.; Kuo, S.-C. *J. Am. Chem. Soc.* **1986**, *108*, 1106. (r) Curran, D. P.; Rakiewicz, D. M. *Tetrahedron* **1985**, *41*, 3943.

(3) For an excellent recent review, see: Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986. See, also: Hart, D. J. *Science (Washington, D. C.)* **1984**, *223*, 883.

(4) Related methods using germanium and mercuric hydrides are common. Germanium hydride: (a) Pike, P.; Hershberger, S.; Hershberger, J. *Tetrahedron Lett.* **1985**, *26*, 6289. (b) Lusztyk, J.; Maillard, B.; Lindsay, D. A.; Ingold, K. U. *J. Am.* Chem. *Soc.* **1983**, *105*, 3578. Mercuric hydride: (c) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *224*, 553. (d) Russell, G. A.; Guo, D. *Tetrahedron Lett.* **1984**, *25*, 5239.

(5) Other important methods to control radical reactions involve the use of allyl (and vinyl) tin reagents and thiohydroxamic acid esters (Barton method). Allyl stannanes: (a) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079. (b) Keck, G. E.; Yates, J. B. *J. Organomet. Chem.* **1983**, *248*, C21. (c) Russell, G. A.; Herold, L. L. *J. Org. Chem.* **1985**, *50*, 1037. (d) Baldwin, J. E.; Kelly, D. R. *J. Chem. Soc., Chem. Commun.* **1985**, 683. Allyl sulfides: (e) Keck, G. E.; Byer, J. H. *J. Org. Chem.* **1985**, *50*, 5442. Allyl sulfones: (f) Smith, T. A. K.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1985**, 897. Leading references to the Barton method: (g) Barton, D. H. R.; Motherwell, W. B. *Heterocycles* **1984**, *21*, 1. (h) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901.

(6) For recent reviews, see: (a) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, **1980**; pp 162-283. (b) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. (c) Surzur, J. M. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982; Vol. 2, Chapter 3 . (d) Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299. (e) The series edited by Kochi is still an outstanding source of relevant mechanistic data. Kochi, J. K. *Free Radicals*; Wiley: New York, 1973. (f) Giese, B. *Angew. Chem., Int. Engl.* **1983**, *22*, 753.

(7) For a review of halogen atom abstraction, see: Danen, W. C. In *Methods in Free Radical Chemistry*; Huyser, E. S., Ed.; Marcel Dekker: New York, 1974; Vol. 5, pp 1-100. Poutsma, M., in ref 6e, Vol. II, p 23. See, also: (a) Hiatt, R.; Benson, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 25. (b) Castelhano, A. L.; Griller, D. *Ibid.* **1982**, *104*, 3655.

(8) The driving force in most work is the formation of a stabilized radical. For some examples, see: (a) Giese, B.; Leining, M. *Chem. Ber.* **1986**, *119*, 444. (b) Fields, D. L., Jr.; Schecter, H. *J. Org. Chem.* **1986**, *51*, 3369. (c) Kuwae, Y.; Kamachi, M.; Hayashi, K.; Viehe, H. G. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2325. (d) Sam, T. W.; Sutherland, J. K.; *J. Chem. Soc., Chem. Commun.* **1971**, 970. (e) Traynham, J. G.; Hsieh, H. H. *J. Org. Chem.* **1973**, *38*, 868. (f) Brown, E. D.; Sam, T. W.; Sutherland, J. K.; Torre, A. *J. Chem. Soc., Perkin Trans 1* **1975**, 2326. (g) Kharasch, M. S.; Skell, P. S.; Fisher, P. *J. Am. Chem. Soc.* **1948**, *70*, 1055. (h) Nakano, T.; Kayama, M.; Matsumoto, H.; Nagai, Y. *Chem. Lett.* **1981**, 415. (i) Kraus, G. A.; Landgrebe, K. *Tetrahedron Lett.* **1984**, *25*, 3939. Kraus, G. A., Landgrebe, K. *Tetrahedron* **1985**, *41*, 4039. Degueil-Castaing, M.; DeJeso, B.; Kraus, G. A.; Landgrebe, K.; Maillard, B. *Tetrahedron Lett.* **1986**, *27*, 5927. (j) Pezechk, M.; Brunetiere, A. P.; Lallemand, J. Y. *Tetrahedron Lett.* **1986**, *27*, 3715.

(9) We use the term "atom transfer" to emphasize the method of control of the radical reaction. Of central importance is the nature of the chain-transfer step. In the tin hydride method, the chain is transferred by hydrogen abstraction from the reagent. In the atom transfer method, the chain is transferred by halogen atom abstraction from the starting halide. Atom transfer methods based on hydrogen atom abstraction from the starting material are also known. For examples and references, see: Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386. Gottschalk, P.; Neckers, D. C. *J. Org. Chem.* **1985**, *50*, 3498.

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(11) General experimental procedure: A solution of alkene (0.62 mmol), alkynyl iodide (1.55 mmol), and hexabutylditin (0.06 mmol) in dry, degassed benzene (1.8 mL) was irradiated for 40 min with a 275-W sunlamp. The temperature was maintained at 80 ± 5 °C by controlling the distance of the lamp from the reaction vessel. If starting alkene remained, additional ditin (0.06 mmol) was added, and irradiation was continued for 40 min. The reaction was concentrated under reduced pressure, and the residue was purified by medium pressure liquid chromatography.

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