information about the topology of the potential surface and show promise as a means of investigating other fundamental reactions.

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Registry No. $ClCO_2CH_3$, 79-22-1; Cl^-, 16887-00-6; $CF_3CO_2CH_3$, 431-47-0.

Stereoselective Chelation-Controlled Reduction of α-Iodo-β-alkoxy Esters under Radical Conditions[1]

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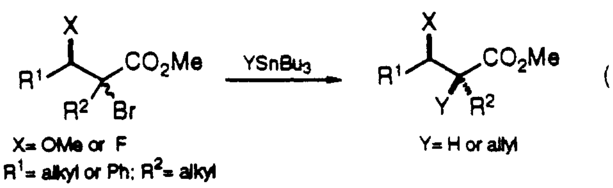
The application of free-radical reactions in organic synthesis has grown enormously during the past decade providing a wealth of useful new chemistry.[2] However, relatively few reports have addressed the problem of stereocontrol in reactions involving acyclic radicals. Very recently it has been shown that chirality transfer can be achieved successfully using chiral auxiliaries[3] or stereogenic centers adjacent to the radical center.[4,5] In this communication we describe an alternative solution to the problem of stereocontrol in acyclic molecules wherein chelation-controlled reductions are performed under radical conditions.

Previously, we reported that the radical-mediated reduction[5b] or allylation[5c] of acyclic β-methoxy-α-halo or β-fluoro-α-halo esters proceeds with good to excellent stereoselectivity (eq 1). To



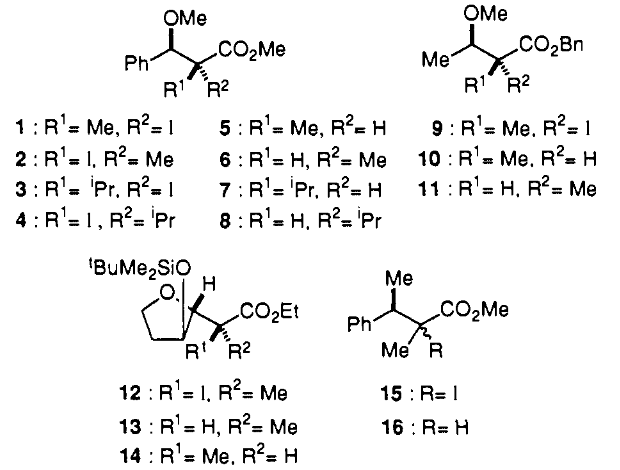


Figure 1.

Scheme I

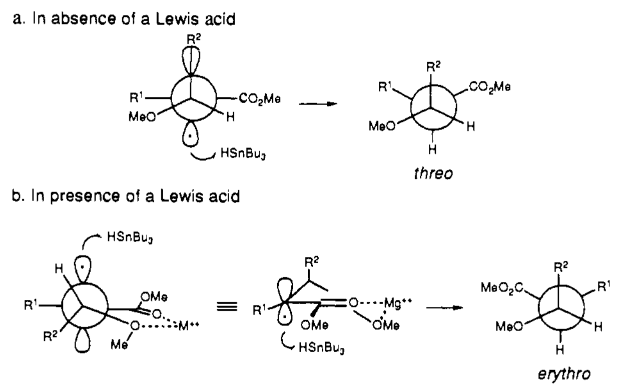


Table I. Reduction of Iodoester **1** with Bu_3SnH in the Presence of Various Lewis Acids

entry	Lewis acid	equiv	ratio[a] (erythro:threo)	yield, %
1			1:>25	90
2	MgI_2	1.0	>25:1	78
3	MgI_2	0.25	25:1	71
4	$MgBr_2 \cdot OEt_2$	1.0	>25:1	84
5	$MgBr_2 \cdot OEt_2$	0.25	>25:1	81
6	$AlCl_3$	1.0	>25:1[b]	75
7	$AlCl_3$	0.24	1:1.8	

[a] Ratios determined by ^1H NMR spectroscopy. [b] Threo diastereomer could not be detected by ^1H NMR spectroscopy.

account for this stereochemical outcome we proposed a transition state as depicted in Scheme Ia.[5b] Consideration of this model led to the hypothesis that a bidentate Lewis acid could alter the structure of the transition state thus changing the stereochemical outcome of the reaction. As shown in Scheme Ib, chelation of the carbonyl and methoxy moieties to a Lewis acid forces the molecule into a conformation which exposes the top face of the radical π system (Newman projection) to hydrogen atom delivery and thus provides access to the erythro manifold.[6]

In order to test this hypothesis, iodo ester **1**[7] was treated with Bu_3SnH in the presence of various Lewis acids. As shown in Table I, excellent erythro selectivities were observed when MgI_2, $MgBr_2 \cdot Et_2O$, or $AlCl_3$ were employed (entries 2, 4, and 6).[8-10]

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(2) (a) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969. (b) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: Oxford, 1986. (c) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753. For reviews discussing radical cyclizations, see: (d) Thebtaranonth, C.; Thebtaranonth, Y. *Tetrahedron* **1990**, *46*, 1385. (e) Curran, D. P. *Synthesis* **1988**, *417*, 489. (f) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (g) Hart, D. J. *Science* **1984**, *223*, 883.

(3) (a) Porter, N. A.; Scott, D. M.; Rosenstein, I. J.; Giese B.; Veit, A.; Zeitz, H. G. *J. Am. Chem. Soc.* **1991**, *113*, 1791 and references cited therein. (b) Porter, N. A.; Wu, W.-X.; McPhail, A. T. *Tetrahedron Lett.* **1991**, *32*, 707 and references cited therein. (c) Curran, D. P.; Shen, W.; Zhang, J.; Heffner, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 6738. (d) Hamon, D. P. G.; Razzino, P.; Massy-Westropp, R. A. *J. Chem. Soc., Chem. Commun.* **1991**, 332. (e) Hamon, D. P. G.; Massy-Westropp, R. A.; Razzino, P. *J. Chem. Soc., Chem. Commun.* **1991**, 722. (f) Stack, J. G.; Curran, D. P.; Rebek, J., Jr.; Ballester, P. *J. Am. Chem. Soc.* **1991**, *113*, 5918.

(4) (a) Hart, D. J.; Huang, H.-C. *Tetrahedron Lett.* **1985**, *26*, 3749. (b) Hart, D. J.; Krishnamurthy, R. *Synlett* **1991**, 412. (c) Hart, D. J.; Huang, H.-C.; Krishnamurthy, R.; Schwartz, T. *J. Am. Chem. Soc.* **1989**, *111*, 7507. (d) Crich, D.; Davies, J. W. *Tetrahedron* **1989**, *45*, 5641. (e) Ogura, K.; Yanagisawa, A.; Fujino, T.; Takahashi, K. *Tetrahedron Lett.* **1988**, *29*, 5387. (f) Crich, D.; Davies, J. W. *Tetrahedron Lett.* **1987**, *28*, 4205. (g) Vassen, R.; Runsink, J.; Scharf, H.-D. *Chem. Ber.* **1986**, *119*, 3492. (h) Henning, R.; Urbach, H. *Tetrahedron Lett.* **1983**, *24*, 5343. (i) Bullard, M.; Zeitz, H.-G.; Giese, B. *Synlett* **1991**, 423. (j) Giese, B.; Bullard, M.; Zeitz, H.-G. *Synlett* **1991**, 425. See also ref 2a.

(5) (a) Guindon, Y.; Anderson, P. C.; Yoakim, C.; Girard, Y.; Berthiaume, S.; Morton, H. E. *Pure Appl. Chem.* **1988**, *60*, 1705. (b) Guindon, Y.; Yoakim, C.; Lemieux, R.; Boisvert, L.; Delorme, D.; Lavallée, J.-F. *Tetrahedron Lett.* **1990**, *31*, 2845. (c) Guindon, Y.; Lavallée, J.-F.; Boisvert, L.; Chabot, C.; Delorme, D.; Yoakim, C.; Hall, D.; Lemieux, R.; Simoneau, B. *Tetrahedron Lett.* **1991**, *32*, 27.

(6) For a discussion of chelated transition states see: Chen, X.; Hortelano, E. R.; Eliel, E. L.; Frye, S. V. *J. Am. Chem. Soc.* **1990**, *112*, 6130.

(7) Vishwakarma, L. C.; Walia, J. S. *J. Indian Chem. Soc.* **1976**, 156.

(8) Compounds **5** and **6** are known. See: Murata, S.; Suzuki, M.; Noyori, R. *Tetrahedron* **1988**, *44*, 4259.

(9) $SnCl_4$ and $EtAlCl_2$ gave only moderate amounts of erythro products. The use of $ZnCl_2$, ZnI_2, $MgCl_2$, or $BF_3 \cdot Et_2O$ gave predominantly the threo isomer.

Table II. Reduction of α-Iodo Esters with Bu_3SnH

entry	iodide	conditions[a]	ratio[b] (erythro:threo)	products (erythro:threo)	yield, %
1	**1**	A	>25:1	**5**:**6**	78[c]
2	**1**	B	1:>25	**5**:**6**	86[d]
3	**2**	A	1:4	**5**:**6**	61[e]
4	**2**	B	1:>25	**5**:**6**	85[d]
5	**3**	A	>25:1	**7**:**8**	79[c]
6	**3**	B	1:24	**7**:**8**	87[d]
7	**4**	A	1:2.3	**7**:**8**	76[e]
8	**9**	A	5:1	**10**:**11**	82[e]
9	**9**	B	1:4	**10**:**11**	80[e]
10	**12**	A	10:1	**13**:**14**[f]	53[c]
11	**12**	B	1:>25	**13**:**14**[f]	93[d]
12	**15**	A	1:2.2	**16**[g]	88[e]
13	**15**	B	1:2.3	**16**[g]	89[e]

[a] A: $HSnBu_3$ (2 equiv), MgI_2 (2 equiv), CH_2Cl_2 (0.04–0.05 M), −50 °C, 1 h, then 0 °C, 30 min. B: $HSnBu_3$ (2 equiv) catalytic AIBN, toluene (0.1 M), −78 °C, $h\nu$ (sunlamp, 275 W). [b] Ratios determined by ^{1}H NMR spectroscopy unless otherwise indicated. [c] Isolated yield of pure erythro isomer. [d] Isolated yield of pure threo isomer. [e] Total isolated yield. [f] Ratio determined by gas chromatographic analysis. [g] Relative stereochemistry not determined.

Interestingly, the use of catalytic amounts of MgI_2 or $MgBr_2{\cdot}Et_2O$ resulted in no loss of diastereoselection (entries 3 and 5) while $AlCl_3$ provides good ratios only if a full equivalent is added (entry 7). In addition, no radical initiator is required for these reactions to proceed, the initiation step probably occurring via a single electron transfer process between Bu_3SnH and the electron-deficient chelate.[11]

Contrary to many radical reductions, the configuration of the substrate iodide has a significant effect on the stereochemical outcome of the reaction (Table II). Iodides in which the alkoxy group and iodo moiety are anti (**1**, **3**, **9**, **12**) show a marked preference for producing erythro products when MgI_2 is present while compounds in which the alkoxy and iodo groups are syn (**2**, **4**)[12] show a modest preference for the threo isomer in the presence of MgI_2. The syn and anti iodides react identically in the absence of MgI_2 producing selectively the threo products (entries 2 and 4).[5b] One could rationalize these results by suggesting that the chelated form of the syn iodide is less reactive than the anti iodide in the initial phase of the reaction (C–I breakage) due to developing $A_{1,2}$ strain in the transition state. In the case of syn iodides, the unchelated pathway would therefore be more energetically favored.

The described chemistry provides a novel approach to control of stereochemistry in acyclic radical reactions[13] and is of potential synthetic utility due to its mildness and the ready availability of the starting materials. We are currently investigating the mechanistic aspects of this transformation, the results of which will be published in a full account of this work.

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Supplementary Material Available: Experimental procedures and spectral data (^{1}H NMR, ^{13}C NMR, IR, MS, analysis and/or HRMS) for compounds **1–16** (11 pages). Ordering information is given on any current masthead page.

(10) Stereochemical assignments for 2-alkyl-3-alkoxy esters have been reported. See: Gouzoules, F. H.; Whitney, R. A. *J. Org. Chem.* **1986**, *51*, 2024.

(11) Tanner, D. D.; Blackburn, E. V.; Diaz, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 1557 and references cited therein.

(12) Obtained by isomerization of **1** ($LiI{\cdot}3H_2O$, THF, reflux, 16 h).

(13) Although the presence of a free radical in this reaction has not been firmly established, one will note that the inclusion of deuterated methanol in the reaction medium could not compete with Bu_3SnH as a hydrogen donor, indicating that a radical is probably involved in the reaction.

Photoreaction of Meldrum's Diazo in Poly(methyl methacrylate) Matrices

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Most photochemical reactions are carried out in solution. In the liquid phase, excited molecules normally are able to explore a variety of accessible conformations before reacting. In the solid state, much of this motion is suppressed. In recent years there has been an extensive effort, nicely reviewed by Scheffer,[1] to study photochemical reactions in organic crystals, where the molecular conformation prior to excitation is the same for each molecule. Very special features appear in the photoreaction of organic molecules dissolved in rigid polymer films. This is a field pioneered by Smets and his group in Belgium[2] and reviewed recently.[3,4] The fundamental characteristic of photoreactions in glassy polymer films is their sensitivity to the distribution of free volume in the film: Below the glass transition temperature (T_g), large-scale motion of the polymer is suppressed. As a consequence, if a reaction of a guest molecule involves a change in conformation, the reaction will occur faster in molecules adjacent to sites of substantial free volume, and the reaction rate and quantum efficiency (Φ_r) will decrease as the reaction proceeds. This is clearly the case with a wide variety of photochromic molecules studied by Smets and others, and this principle has been employed by Horie[5a] and by Torkelson[5b] as a means of mapping out the free volume distribution in amorphous polymer films below T_g. It is not surprising that most photoreactions have substantially lower Φ_r values in rigid films than in solution. There are a few rare examples of reactions that have higher Φ_r values in polymer films, one set involving proton tautomerism in benzoylacetanilides,[6] held in the proper geometry by intramolecular hydrogen bonding, and one involving ring closure of an imine oxide to an oxazirine.[7]

This paper describes the photochemistry of Meldrum's diazo (**1**) in poly(methyl methacrylate) (PMMA) films at 22 °C. **1** is of interest to organic chemists because of the question of whether its Wolff rearrangement involves the singlet carbene as a discrete intermediate.[8,10] **1** and its derivatives are also of interest in the microelectronic area since they display many of the ideal characteristics ($\lambda_{max} \approx 250$ nm, transparent photoproducts) of photoactive additives for deep UV photoresists. Effective resists have been reported for **1** in Novolac films,[11] and irradiation of **1** in PMMA films causes those films to dissolve much faster upon

(1) Scheffer, J. R. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH Publishers: New York, 1991.

(2) Smets, G. *Adv. Polym. Sci.* **1983**, *50*, 17.

(3) (a) Horie, K.; Mita, I.; *Adv. Polym. Sci.* **1989**, *88*, 77. (b) Farid, S.; Martic, P. A.; Daly, R. C.; Thompson, D. R.; Specht, D. P. Hartman, S. E.; Williams, J. L. R. *Pure Appl. Chem.* **1979**, *51*, 241.

(4) Guillet, J. E. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, 1984; Chapter 5.

(5) (a) Naito, T.; Horie, K.; Mita, I.; *Macromolecules* **1991**, *24*, 2907. (b) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1987**, *20*, 2241.

(6) Petkov, I.; Dodov, N.; Markov, P. *J. Photochem. Photobiol. A* **1990**, *54*, 119.

(7) Smets, G. J.; Matsumoto, S. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2983.

(8) Jones, M., Jr.; Ando, W.; Hendrick, M. E.; Kulczycki, A., Jr.; Howley, P. M.; Hummel, K. F.; Melament, D. S. *J. Am. Chem. Soc.* **1972**, *94*, 7469.

(9) Kammula, S. L.; Tracer, H. L.; Shelvin, P. B.; Jones, M., Jr. *J. Org. Chem.* **1977**, *42*, 2931.

(10) Regitz, M. *Diazo Compounds*; Academic Press Inc.: London, 1985; Chapter 4.

(11) Grant, B. D.; Clecak, N. J.; Twieg, R. J.; Willson, C. G. *IEEE Trans. Electron Devices* **1981**, *28*, 1300.

0002-7863/91/1513-9702$02.50/0