# Mn(III)-Based Oxidative Free-Radical Cyclizations of Unsaturated Ketones

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Mn(III)-based oxidative free-radical cyclization of unsaturated ketones is a versatile synthetic procedure with broad applicability. For example, oxidation of cyclopentanone **1a** with 2 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in AcOH at 80 °C for 1.5 h affords 75% of bicyclo[3.2.1]oct-3-en-8-one **8a** and 15% of bicyclo[3.2.1]oct-2-en-8-one **9a**. Bridged bicyclic ketones that cannot enolize further are isolated in good yield. Monocyclic $\beta,\gamma$-unsaturated ketones that can enolize are oxidized further to give $\gamma$-acetoxy enones. The formation of bicyclo[3.3.1]non-2-en-9-one (**57a**) in 52% yield from 2-allylcyclohexanone (**56a**) suggests that kinetically controlled enolization is the rate-determining step in α-keto radical formation. A wide variety of examples delineating the scope, limitations, and stereoselectivity of this reaction are presented.

During the past decade, Mn(III)-based oxidative free-radical cyclizations have been developed into a versatile protocol for the formation of highly functionalized products from simple precursors.[1] These cyclizations have been initiated by reaction of relatively acidic compounds, such as 1,3-diketones, acetoacetates, malonates, and α-sulfinyl or α-nitro ketones, with $Mn(OAc)_3$ to form Mn(III) enolates, which undergo electron transfer to give Mn(II) and radicals. The Mn(III)-based oxidative free-radical addition of simple symmetrical ketones to simple alkenes is well known.[1c−e] In these reactions, the ketone must be used in large excess to prevent further oxidation of the product. Accordingly, the reported yields are based on oxidant consumed, and these reactions are of limited preparative value. Oxidative free-radical cyclizations of unsaturated ketones have not been examined, presumably because of anticipated problems with both the regioselectivity of radical formation and further oxidation of the cyclic ketone products when the starting ketone is too valuable to use in large excess.

**Cyclization of 5-Hexenyl Radicals. Oxidative Cyclization of 1-Allyl-2-oxocycloalkanecarboxylates 1a−d.** We have found that Mn(III)-based oxidative free-radical cyclization of unsaturated ketones is in fact a versatile synthetic procedure with broad applicability.[2] For instance, reaction of cyclopentanone **1a** as a 0.1 M solution in AcOH with 2.25 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ for 1.5 h at 80 °C affords 75% of bicyclo[3.2.1]oct-3-en-8-one **8a**,[3] 15% of bicyclo[3.2.1]-oct-2-en-8-one **9a**, and <1% of cyclopentenone **6a**. The slow step appears to be the formation of Mn(III)-enolate **2a**,[4a,b] which undergoes electron transfer with loss of Mn(II) to give α-keto radical **3a**. 6-*endo*-Cyclization affords radical **4a**, which is oxidized by Cu(II) to give 90% of a 5:1 mixture of **8a** and **9a**. We have previously observed that Cu(II) oxidizes alkyl radicals selectively to afford the least hindered alkene.[5] Since the double bonds in both **8a** and **9a** are disubstituted, oxidative elimination apparently selectively removes the least hindered proton, which is adjacent to the bridgehead hydrogen rather than the ester group, to give predominantly **8a**. A trace of α,$\beta$-unsaturated enone **6a** is obtained from oxidation of α-keto radical **3a**. Similar reactions carried out at 60 °C for 24 h and 25 °C for 11 d provide only 55% and 23% of similar mixtures of products, respectively. Oxidation of **1a** in ethanol or methanol at reflux provides a small amount of recovered starting material and polymeric products; reaction of **1a** in benzene gives products in yields comparable to that in acetic acid, but the reaction requires 68 h to go to completion. Thus, the optimal conditions are 80 °C in acetic acid.

Cyclohexanone **1b** reacts more slowly (16 h, 80 °C) than **1a** to give a similar mixture of 66% of bicyclo[3.3.1]non-3-en-9-one **8b**,[6] 7% of bicyclo[3.3.1]non-2-en-9-one **9b**,[7] and 4% of 6-methylenebicyclo[3.2.1]octan-8-one **10b**,[8] which is formed by 5-*exo*-cyclization. Heiba and Dessau have reported that the rate-determining step in α-keto radical formation from ketones involves reaction of Mn(III) with the enol or enolate.[4] The rate is independent of Mn(III) concentration, first order in ketone concentration, and accelerated by acetate ion, which suggests that base-catalyzed enolization is the rate-determining step of the reaction. The observation that cyclohexanone **1b** reacts 10 times slower than cyclopentanone **1a** is consistent with this analysis, since enolization of cyclohexanone is about 10 times slower than enolization of cyclopentanone.[9]

Similarly, cycloheptanone **1c** (85 h, 80 °C) gives 21% of bicyclo[4.3.1]dec-7-en-10-one **8c**, 1% of bicyclo[4.3.1]-non-8-en-10-one **9c**, and 22% of 7-methylenebicyclo[3.2.1]-nonan-9-one **10c**. As the ring size of the ketone in-

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(1) For reviews see: (a) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339. (b) Iqbal, J.; Bhatia, B.; Nayyar, N. K. *Chem. Rev.* **1994**, *94*, 519. (c) Melikyan, G. G. *Synthesis* **1993**, 833. (d) Badanyan, Sh. O.; Melikyan, G. G.; Mkrtchyan, D. A. *Russ. Chem. Rev.* **1989**, *58*, 286; *Uspekhi Khim.* **1989**, *58*, 475. (e) de Klein, W. J. In *Organic Synthesis by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H., Eds.; Plenum Press: New York, 1986; pp 261−314.

(2) For preliminary communications on portions of this work see: (a) Snider, B. B.; McCarthy Cole, B. *J. Org. Chem.* **1995**, *60*, 5376. (b) Snider, B. B.; McCarthy, B. A. In *Benign by Design. Alternative Chemical Synthesis for Pollution Prevention*; Anastas, P., Farris, C., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1994; Chapter 7.

(3) Buchanan, G. L.; Curran, A. C. W.; McCrae, J. M.; McLay, G. W. *Tetrahedron* **1967**, *23*, 4729.

(4) (a) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 524. (b) Fristad, W. E.; Peterson, J. R. *J. Org. Chem.* **1985**, *50*, 10. (c) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 2888. (d) Dessau, R. M.; Heiba, E. I. *J. Org. Chem.* **1974**, *39*, 3457.

(5) Snider, B. B.; Kwon, T. *J. Org. Chem.* **1990**, *55*, 1965.

(6) Colvin, E. W.; Parker, W. *J. Chem. Soc.* **1965**, 5764.

(7) Kende, A. S; Roth, B.; Sanfilippo, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 1784. Kende, A. S.; Wustrow, D. J. *Tetrahedron Lett.* **1985**, *26*, 5411.

(8) Berkowitz, W. F.; Wilson, P. J. *J. Org. Chem.* **1991**, *56*, 3097.

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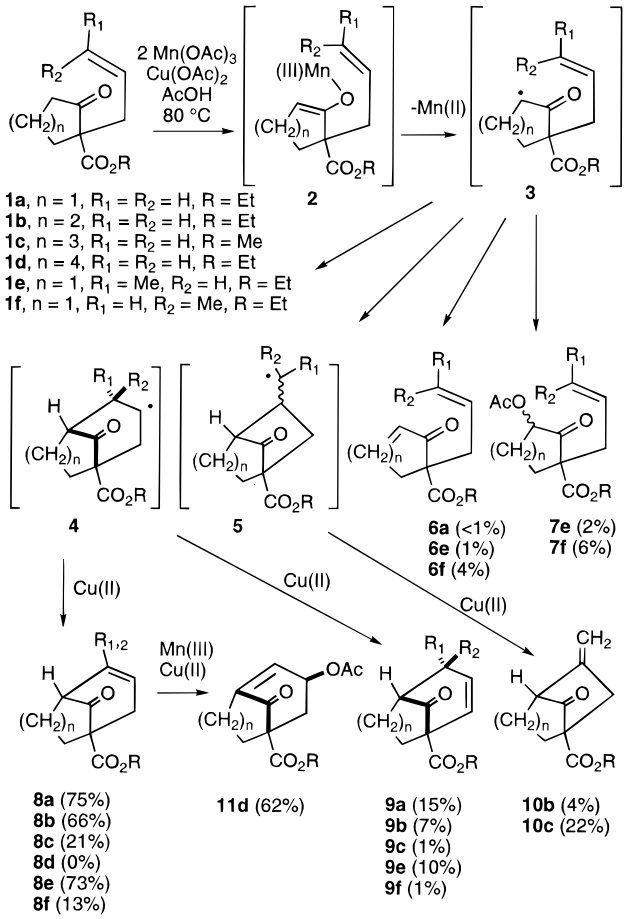



creases, 5-*exo*-cyclization competes more effectively with 6-*endo*-cyclization. These reactions proceed in synthetically useful yield since ketones **1a**−**c** can enolize in only one direction and bridged bicyclic ketones **8a**−**c**, **9a**−**c**, and **10b,c** are not susceptible to further oxidation because they cannot enolize.

Cylooctanone **1d** behaves very differently (8 equiv of $Mn(OAc)_3 \cdot 2H_2O$, 1 equiv of $Cu(OAc)_2 \cdot H_2O$, 226 h, 80 °C), giving 62% of 9-acetoxybicyclo[5.3.1]oct-7-en-11-one **11d**. The larger ring permits enolization[10] of the anticipated major product **8d** to give a Mn(III) enolate with an *E*-double bond in an eight-membered ring. Oxidation of the allylic radical to the cation and reaction of the cation with solvent gives acetate **11d** as a single stereoisomer resulting from attack of acetate on the less hindered *exo*-face. The couplings to C*H*OAc ($J$ = 6.5, 6.3, 4.8 Hz) correspond to that calculated for the exo isomer ($J$ = 8.6, 7.4, 4.2 Hz), but not for the endo isomer ($J$ = 7.3, 3.2, 1.2 Hz).[11] The facile oxidation of $\beta,\gamma$-unsaturated enones to $\gamma$-acetoxy-$\alpha,\beta$-unsaturated enones by Mn(III) and Cu(II) has been extensively studied.[12]

**Oxidative Cyclization of Ethyl 1-(2-Butenyl)-2-oxocyclopentanecarboxylates (1e,f).** 2(*Z*)-Butenylcyclopentanone **1f** behaves very differently than the *E*-isomer **1e**, indicating that the double bond stereochemistry has a remarkable effect on the 6-*endo*-cyclizations of α-keto radicals. The *E*-isomer **1e** reacts similarly to **1a**, giving 73% of **8e**[13] and 10% of **9e**. Trace amounts of cyclopentenone **6e** and α-acetoxycyclopentanone **7e** are obtained from oxidation of α-keto radical **3e**. The stereochemistry of **9e** was assigned based on the olefinic hydrogen absorptions at $\delta$ 6.01 ($J$ = 9.3, 2.6 Hz) and $\delta$ 5.45 ($J$ = 9.3, 2.1, 1.2 Hz). The allylic coupling of 2.6 Hz and the vicinal coupling of 2.1 Hz indicate that the allylic methine hydrogen is pseudoaxial.

We were surprised to find that oxidation of **1f** with 3 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in AcOH at 80 °C for 2 h only gives 13% of **8e** = **8f** along with 4% of enone **6f** and 6% of a 1:1 mixture of acetates **7f**. A trace amount of **9f** (≈1%) was also detected in the $^1$H NMR spectrum of the crude mixture of products. This compound displays an olefinic absorption at $\delta$ 6.05 ($J$ = 9.9) and a doublet at $\delta$ 1.11 ($J$ = 7.1), indicating that it is the stereoisomer of **9e**.

The difference in the yield of the bicyclic products from the *Z*- and *E*-isomers **1e** and **1f** initially led us to suspect that manganese enolates **2e** and **2f** cyclize to bicyclic radicals **4e** and **4f**, respectively, without the intermediacy of $\beta$-keto radicals **3e** and **3f**. However, a control experiment established that both the *Z*- and *E*-isomers are oxidized by Mn(III) at the same rate. Ketones **1e** and **1f** were simultaneously added to separate, stirred mixtures of 2 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in acetic acid at 80 °C, and the reactions were then monitored for the complete consumption of Mn(III) as indicated by the solution turning bright blue. All the Mn(III) was consumed in 75 min in both reactions. GC analysis indicated that 10% of **1e** and 33% of **1f** remained.

Radicals **3e** and **3f** are probably intermediates since the rate of oxidation of **1e** and **1f** by Mn(III) should be the same if enolization is the rate-limiting step. The reaction rates would be very different if cyclization of Mn(III) enolate **2e,f** to give **4e,f** was the rate-determining step. Since **1e** and **1f** are oxidized by Mn(III) to **3** at the same rate, the methyl group of the (*Z*)-crotyl substrate must sterically hinder 6-*endo*-addition of the α-keto radical of **3f** to the double bond, so that **3f** gives more **6f**, **7f**, and polymer.

**Oxidative Cyclization of 1-(2-Butenyl)-2-oxocyclohexanecarboxylates 12a,b.** The oxidative cyclization of 2(*E*)-butenyl-substituted ethyl 2-oxocyclohexanecarboxylate **12a** with 2.25 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in AcOH at 80 °C for 16 h provides 18% of **16**, <1% of **17**, 13% of **18**, 32% of **20**,[14] 7% of **21a**, 7% of **23a**, and 2% of **24a**. α-Keto radical **13a** undergoes 5-*exo*-cyclization to provide radicals **14** and **15** and 6-*endo*-cyclization to afford radical **19a**. Oxidation of **14** and **15** by Cu(II) gives the less hindered terminal alkenes **16** and **18**, respectively, and a trace of **17**. Oxidation of radical **19a** by Cu(II) provides a 4:1 mixture of **20** and **21a**, while a 1,5-hydrogen shift gives radical **22a**, which is oxidized by Cu(II) to afford **23a** and **24a**. The 1,5-hydrogen shift is particularly facile since the hydrogen is in close proximity to the radical center. Related examples of cyclooctyl radicals undergoing a similar 1,5-shift are known.[15]

(9) Cyclopentanone is deprotonated by triethylamine in DMF/water 10 times faster than cyclohexanone: (a) Toullec, J. Enolisation of Simple Carbonyl Compounds and Related Reactions. In *Advances in Physical Organic Chemistry*; Gold V., Ed.; Academic Press: London, 1982; Vol. 18, p 1. (b) Shechter, H.; Collis, M. J.; Dessy, R.; Okuzumi, Y.; Chen, A. *J. Am. Chem. Soc.* **1962**, *84*, 2905.

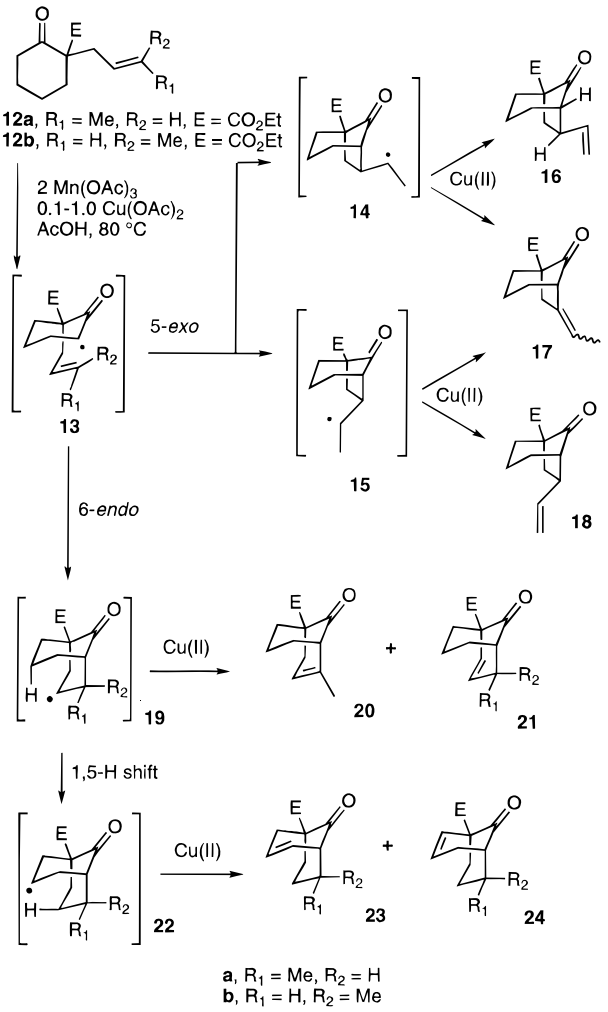
(10) Buchanan, G. L.; Jamieson, G. *Tetrahedron* **1972**, *28*, 1123 and 1129.

(11) Model version KS 2.99 obtained from Prof. Steliou, Boston University, was used for MM2 calculations.

(12) Breuilles, P.; Uguen, D. *Bull. Soc. Chim. Fr.* **1988**, *88*, 705.

(13) Evans, E. H.; Hewson, A. T.; March, L. A.; Nowell, I. W.; Wadsworth, A. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, 137.

(14) (a) Erman, W. F.; Kretschmar, H. C. *J. Org. Chem.* **1968**, *33*, 1545. (b) Foote, C. S.; Woodward, R. B. *Tetrahedron* **1964**, *20*, 687.



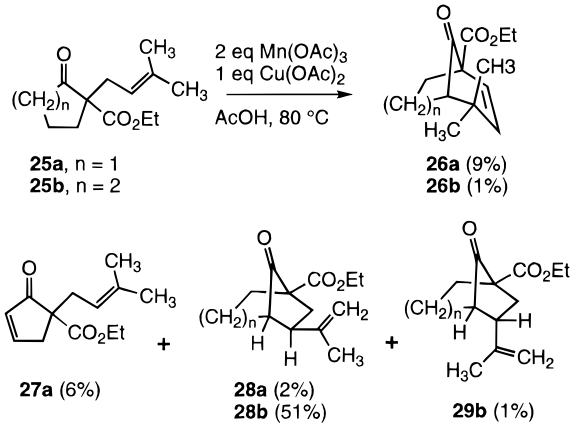

More of the rearrangement products **23a** and **24a** should be formed if less Cu(II) is used, since the oxidation of **19a** is a second-order process and the rearrangement of **19a** to **22a** is a first-order process. As anticipated, oxidation of **12a** with 2.25 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and only 0.1 equiv of $Cu(OAc)_2 \cdot H_2O$ provides 15% of **16**, 10% of **18**, 26% of **20**,[14] 6% of **21a**, 18% of **23a**, and 5% of **24a**. As expected, the yields of rearrangement products **23a** and **24a** increase significantly, at the expense of **20** and **21a**, which confirms that they are obtained from oxidation of **22a**, which is formed from radical **19a** by a 1,5-hydrogen shift.

Oxidation of *Z*-substrate **12b** with 2.25 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in AcOH at 80 °C for 16 h provides 46% of **16**, <1% of **17**, 5% of **18**, 2% of **20**, 2% of **21b**, 2% of **23b**, and 1% of **24b**. As observed in the oxidative cyclization of **1f**, the *Z*-methyl group of **12b** obstructs 6-*endo*-addition of the radical to the double bond so that 5-*exo*-cyclization becomes the major reaction pathway, providing bicyclo[3.2.1]octanone **16** as the major product in synthetically useful yield. The methyl group stereochemistry also affects the stereochemistry of the 5-*exo*-cyclization. *E*-Isomer **12a** provides a 1.4:1 mixture of **16** and **18**, while the *Z*-isomer **12b** provides a 9:1 mixture of **16** and **18** indicating that the *Z*-methyl group hinders the 5-*exo*-cyclization that gives radical **15** with an *endo*-methyl group. Oxidative elimination of cyclohexyl radicals **19a** and **22a** selectively removes the least hindered proton, which is adjacent to the bridgehead hydrogen rather than the ester group, to give predominantly **20** and **23a**, as we observed in the oxidation of **4b**.

The structures of the products were assigned by analysis of the $^1H$ NMR spectral data. The allylic methine hydrogen of **16** at $\delta$ 2.66 ($J$ = 4.6, 8.3, 9.1 Hz) is coupled to the vinyl hydrogen with $J$ = 8.3 Hz and to the adjacent methylene group with $J$ = 4.6 and 9.1 Hz. Therefore, the coupling to the bridgehead hydrogen is less than 1 Hz, which is consistent with that calculated for the *endo* allylic hydrogen of **16** (dihedral angle calculated[11] to be 94°) but not for the *exo* allylic hydrogen of **18** (dihedral angle calculated[11] to be 35°). The structures of products **21a,b**, **23a,b**, and **24a,b** were assigned by analogy to **8b** and **9b**.[16] The stereochemistry of **21a** was assigned analogously to that of **9e**; the allylic coupling of 2.3 Hz and the vicinal coupling of 2.7 Hz indicate that the allylic methine hydrogen is pseudoaxial.

**Oxidative Cyclization of 1-Prenyl-2-oxocycloalkanecarboxylates 25a,b.** Treatment of **25a** with 3 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in AcOH at 80 °C for 2.5 h provides only 9% of bicyclo[3.2.1]octenone **26a** along with 2% of bicyclo[2.2.1]heptanone **28a** and 6% of cyclopentenone **27a**. α-Ketocyclopentyl radicals such as **3a** and **3e** undergo 6-*endo*-cyclization if there is no *Z*-substituent on the double bond. If there is a *Z*-substituent on the double bond as in **3f**, 6-*endo*-cyclization is retarded and 5-*exo*-cyclization leads to strained products. Therefore, bicyclic products are obtained in low yield and oxidation to enone **27a** and polymerization are the major processes.

The 5-*exo*-cyclization of α-ketocyclohexyl radicals is more facile, so that 5-*exo*-cyclization of radical **13b** proceeds in good yield since 6-*endo*-cyclization is retarded by the cis substituent on the alkene. As expected, oxidative cyclization of 1-prenyl-2-oxocyclohexanecarboxylate **25b** with 2.5 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in AcOH at 80 °C for 18 h provides 51% of **28b**, 1% of **29b**, and 1% of **26b**. The stereochemistry of **28b** was assigned on the basis of the ≈0 Hz coupling constant between the allylic methine at $\delta$ 2.67 and the bridgehead hydrogen, which is consistent with that expected for the allylic *endo* hydrogen.

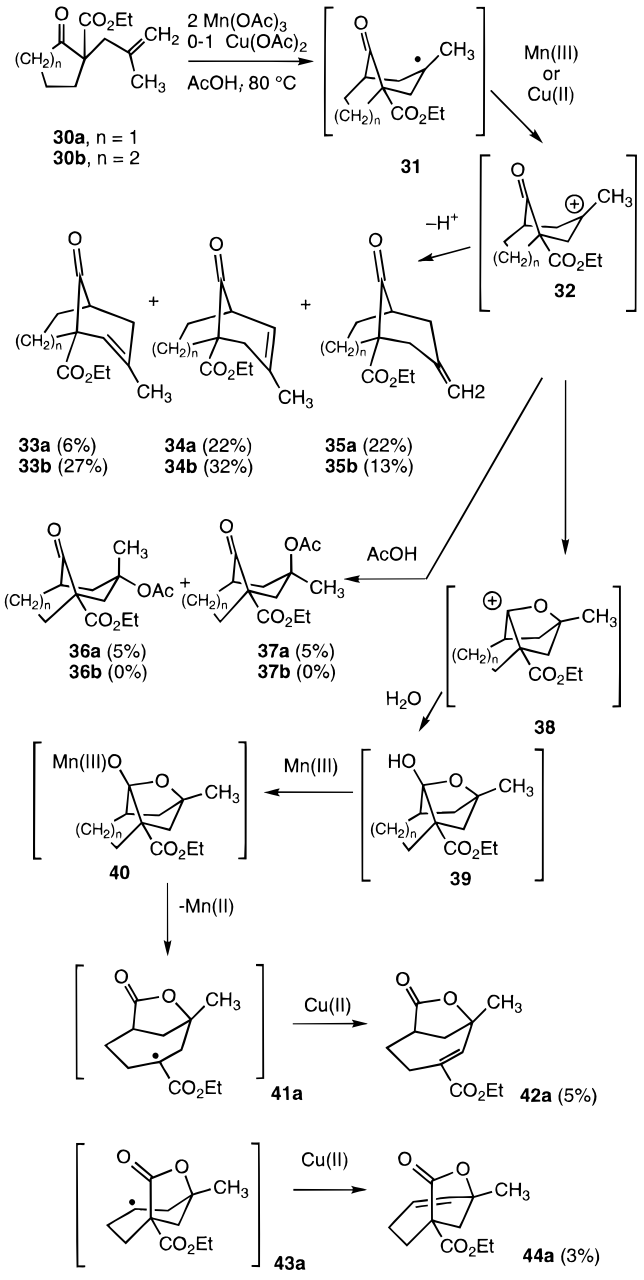



**Oxidative Cyclization of 1-Methallyl-2-oxocycloalkanecarboxylates 30a,b**. Oxidative cyclization of **30a**

(15) For examples of 1,5-hydrogen shifts in cyclooctyl systems see: (a) Meek, J. S.; Fowler, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 1967. (b) Matsumoto, H.; Nakano, T.; Takasu, K.; Nagai, Y. *J. Org. Chem.* **1978**, *43*, 1734.

(16) For further discussion of structure determination of the cyclization products see: Cole, B. M. Ph.D. Thesis, Brandeis University, 1995. Han, L. Ph.D. Thesis, Brandeis University, 1996.

gives complex product mixtures typical of reactions that yield tertiary radicals, which are oxidized to cations by either Mn(III) or Cu(II). Treatment of **30a** with 2.25 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in AcOH for 1.5 h at 80 °C provides 6% of **33a**, 22% of **34a**, 22% of **35a**, 5% of acetate **36a**, 5% of acetate **37a**, 5% of lactone **42a**, and 3% of lactone **44a**. Bicyclic radical **31a** is oxidized by Mn(III) or Cu(II) to tertiary cation **32a**. Loss of a proton affords alkenes **33a**, **34a**, and **35a** without the regiocontrol typical of Cu(II) oxidation of secondary radicals. Addition of acetate to cation **32a** provides acetates **36a** and **37a**. Since bicyclic radical **31a** is tertiary, it can be oxidized to cation **32a** by both Mn(III) and Cu(II). Accordingly, similar results are obtained without $Cu(OAc)_2 \cdot H_2O$.




The stereochemistry of acetates **36a** and **37a** was assigned on the basis of the chemical shift of the methyl groups. MM2 calculations[11] clearly show that both stereoisomers exist primarily in a boat conformer as shown. The calculated distance between the ketone and the *exo*-substituent is approximately 2.5 Å; therefore, the acetate of **37a** and the methyl group of **36a** are shielded by the ketone. The acetate of **37a** absorbs upfield at $\delta$ 1.93 as compared to **36a** ($\delta$ 2.07), while the methyl group of **36a** absorbs upfield at $\delta$ 1.59 as compared to **37a** ($\delta$ 1.69).

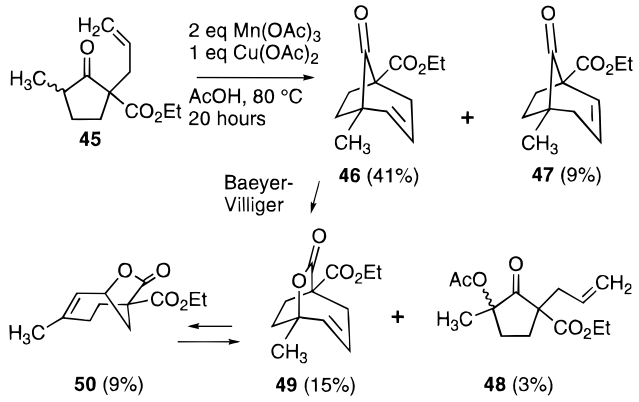
The structures of the unexpected products **42a** and **44a** were assigned on the basis of their $^1$H and $^{13}$C NMR and IR spectral data. Lactone **42a** displays signals at $\delta$ 179.4 and $\delta$ 167.7 in the $^{13}$C NMR spectra and absorptions at 1776 and 1710 $cm^{-1}$ in the IR spectra, indicating the presence of a $\gamma$-lactone and an $\alpha,\beta$-unsaturated ester, but not a cyclopentanone. Although only partial $^{13}$C NMR data were obtained for **44a**, we were able to establish that it contains a $\gamma$-lactone and saturated ester on the basis of the absorptions at 1769 and 1737 $cm^{-1}$ in the IR spectra. A plausible mechanism involves addition of the carbonyl oxygen to the cation of **32a** to give cation **38a**, which is attacked by adventitious water to provide lactol **39a**. Oxidative fragmentation of Mn(III) alkoxide **39a**, as we have previously observed for cyclobutanols[17] and strained cyclopentanols,[18] gives radicals **41a** and **43a**, which are oxidized by Cu(II) to give lactones **42a** and **44a**. The regioselectivity of the oxidative elimination leading to **42a** and **44a** (loss of the more hindered proton) is opposite to what we have usually observed (loss of the least hindered proton). It is possible that Cu(II) coordinates to the lactone or that the electron-withdrawing effect of the lactone makes the adjacent proton more acidic.

Oxidative cyclization of cyclohexanone **30b** with 2.25 equiv of $Mn(OAc)_3$ and 1 equiv of $Cu(OAc)_2$ in AcOH at 80 °C for 18 h affords 27% of **33b**,[19] 32% of **34b**,[19] 13% of **35b**, and 2% of the monocyclic $\alpha'$-acetoxy ketone. Apparently, loss of a proton to give **33b**−**35b** is the exclusive reaction of bicyclo[3.3.1]nonyl cation **32b**, in contrast to bicyclo[3.2.1]octyl cation **32a**, which loses a proton to give **33a**−**35a**, reacts with acetate to give **36a** and **37a**, or cyclizes leading eventually to lactones **42a** and **44a**. Molecular mechanics calculations indicate that bicyclo[3.3.1]nonyl acetates **36b** and **37b** are relatively more strained (compared to bicyclo[3.3.1]nonenes **33b**−**35b**) than bicyclo[3.2.1]octyl acetates **36a** and **37a** (compared to bicyclo[3.3.1]octenes **33a**−**35a**), so that loss of a proton from **32b** is the exclusive reaction. If **39b** were formed, oxidative ring cleavage would not be expected because cyclohexanols do not undergo Mn(III)-based oxidative fragmentations.[18]

**Oxidative Cyclization of 5-Methylcyclopentanone 45.** All of the examples discussed above involve formation of the Mn(III) enolate by loss of a proton from a methylene group. Oxidative cyclization of **45** was examined in order to determine if substrates with a methine hydrogen are usable. Treatment of **45** with 3 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in acetic acid at 80 °C for 20 h provides 41% of **46**, 9% of **47**, 3% of acetate **48**, and 24% of a 2:3 mixture of lactones **50** and **51**. Although **45** was employed as a 1:1 mixture of diastereomers, each isomer is oxidized to the same tertiary α-keto radical, which undergoes 6-*endo*-cyclization exclusively. Oxidation of the resulting bicyclic radical by Cu(II) provides a 4:1 mixture of bicyclo[3.2.1]-octanones **46** and **47**. The structures of **46** and **47** were

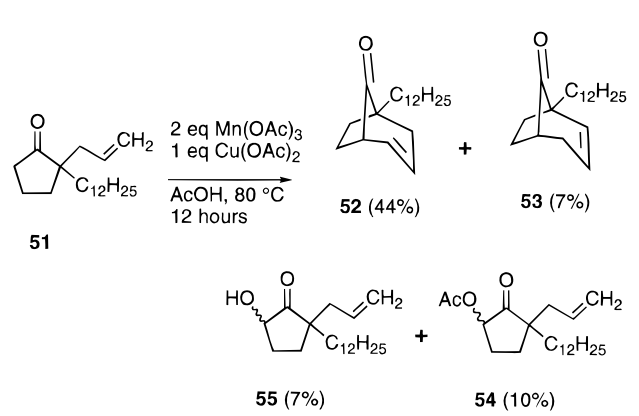
(17) Snider, B. B; Vo, N. H.; Foxman, B. M. *J. Org. Chem.* **1993**, *58*, 7228
(18) Snider, B. B.; O'Neil, S. V. Unpublished results.
(19) Kende, A. S.; Schneider, J. A. *Synth. Commun.* **1979**, *9*, 419.

established by comparison of their $^1$H NMR spectral data to those of **8a** and **8b**. As expected, enolization of the methine hydrogen of **45** is slower than loss of one of the methylene hydrogens of **1a** so that the reaction requires 20 h rather than 1.5 h. Oxidative elimination by Cu(II) shows modest preference for abstraction of a proton from the methyl side rather than the ester side of the ring, possibly indicating electronic as well as steric control of the Cu(II) oxidative elimination of secondary radicals to alkenes.

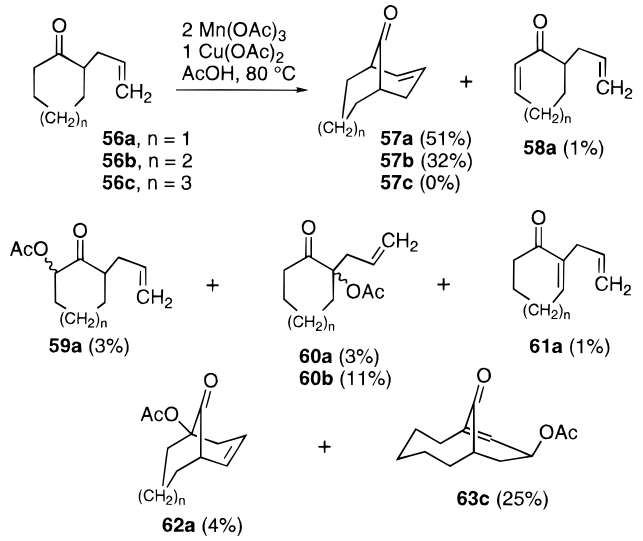



Lactones **49** and **50** were isolated as an inseparable mixture. The IR spectrum shows two carbonyl stretchings at 1771 and 1731 cm$^{-1}$, indicating the presence of a $\gamma$-lactone and an ester group. These lactones are obtained from a Baeyer−Villiger-type oxidation of **46**. Since a tertiary allylic group will migrate more readily than a secondary allylic group, **46** undergoes Baeyer−Villiger oxidation to give **49** while the analogue without the methyl group, **8a**, is stable. Allylic lactone **49** equilibrates with **50** in AcOH at 80 °C by either a [3,3]-sigmatropic rearrangement or ring opening and closure.

**Oxidative cyclization of 2-allyl-2-dodecylcyclopentanone (51)** with 3 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in acetic acid at 80 °C for 12 h gives bicyclo[3.2.1]octenones **52** (44%) and **53** (7%), α-acetoxy ketone **54** (10%), and α-hydroxy ketone **55** (7%), indicating that the ester group is not needed for the success of this sequence. The reaction is about 10 times slower than the oxidative cyclization of **1a**, suggesting that the α-ester group makes the α′-proton of **1a** more acidic than that of **51**.




**Oxidative Cyclization of 2-Allylcycloalkanones 56a−d.** We believed that 2-allylcycloalkanones **56a−c** should be suitable substrates since enolization, the rate-determining step, should occur selectively at the less substituted carbon. Oxidative cyclization of 2-allylcyclohexanone (**56a**) with 4 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in a 0.5 M solution of KOAc in acetic acid at 80 °C for 24 h provides bicyclo[3.3.1]non-2-en-9-one (**57a**)[14] (51%), enone **58a** (1%), and α-acetoxy ketone **59a** (3%), which are all formed by enolization to the kinetically favored methylene side of ketone **56a**. Enolization of the more hindered methine hydrogen affords a tertiary radical that is oxidized to give enone **61a**[20] (1%) and α-acetoxy ketone **60a** (3%). Further oxidation of either acetoxy ketone **59a** or **60a** leads to bicyclic acetoxy ketone **62a** (4%). The reaction proceeds similarly in the absence of potassium acetate, but is less reproducible.

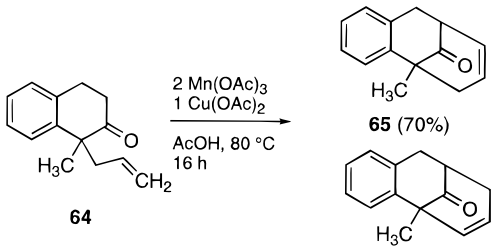


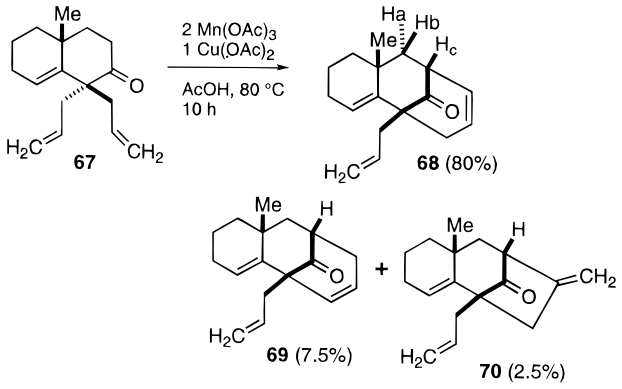

Similarly, oxidative cyclization of 2-allylcycloheptanone (**56b**) with 4 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in acetic acid at 80 °C for 60 h affords 32% of bicyclo[4.3.1]dec-8-en-10-one (**57b**), 11% of α-acetoxy ketone **60b**, and 10% of recovered **56b**. Cycloheptanone **56b** reacts slower than cyclohexanone **56a** and undergoes enolization less selectively at the methylene carbon. Oxidative cyclization of 2-allylcyclooctanone (**56c**) with 6 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in acetic acid at 80 °C for 42 h affords 25% (36% based on recovered **56c**) of 9-*exo*-acetoxybicyclo[5.3.1]undec-10-en-11-one (**63c**). As in the cyclization of **1d** to **11d**, the initially formed bicyclic product **57c** enolizes,[10] and the resulting dienolate is oxidized to an allylic radical that is oxidized to acetate **63c**.

**Oxidative Cyclization of Bicyclic Ketones.** Oxidative cyclization of bicyclic ketones **64** and **67** leads efficiently to tricyclic ketones **65** and **68**. Tetralone **64** cyclizes as expected to give a 14:1 mixture of **65** and **66** in 75% yield with selective formation of the less hindered alkene. Oxidative cyclization of **67** proceeds in high yield, affording 80% of **68**, 7.5% of **69**, and 2.5% of **70**. The radical obtained by enolization and oxidation of octalone **67** could cyclize to either allyl group. The ring fusion hydrogen, $H_c$, of the major product **68** absorbs at $\delta$ 2.92, $J_{Ha,Hc} = 0$ Hz, $J_{Hb,Hc} = 9.5$ Hz, $J_{=CH,Hc} = 5.4$ Hz. These values correspond very closely to those calculated[11] for **68** ($J = 1.0, 8.8, 4.6$ Hz) and are quite different from those calculated for the diastereomer ($J = 5.1, 4.5, 2.5$ Hz). Apparently, the α-keto radical cyclizes exclusively to the α-allyl group with the cyclohexanone in the boat confor-

(20) Taber, D. F. *J. Org. Chem.* **1976**, *41*, 2649.

mation. Cyclization through the chair conformation would occur on the $\beta$-allyl group to give the less stable diastereomer of **68**. This is not observed due to severe steric interactions between the methyl group and the three-carbon bridge in the cyclization transition state.

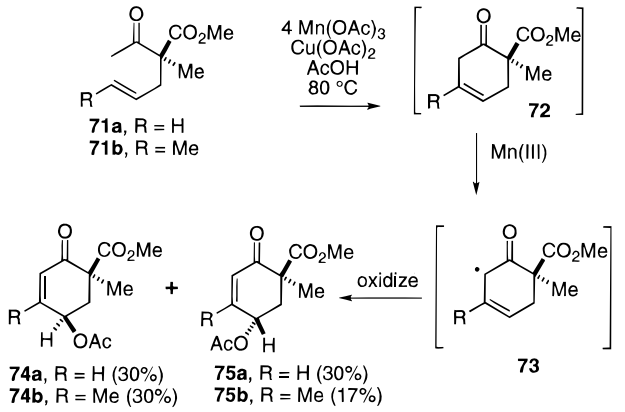



**Oxidative Cyclization of α-Disubstituted Acetoacetates 71a,b and Acetylbutyrolactones 76a,b.** The initial products of the oxidative cyclization of **71a,b** are 3-cyclohexenones **72a,b** that are rapidly oxidized by Mn(III) to provide $\gamma$-acetoxy-$\alpha,\beta$-unsaturated ketones. Treatment of **71a** with 6 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in AcOH for 48 h at 80 °C gives 60% of a 1:1 mixture of **74a** and **75a**. Oxidative cyclization of methyl ketone **71a** should give $\beta,\gamma$-unsaturated ketone **72a**, which is not isolated. 3-Cyclohexenone **72a** is oxidized rapidly to radical **73a** because $\beta,\gamma$-unsaturated ketone **72a** is more acidic than **71a**. Oxidation of radical **73a** provides $\gamma$-acetoxy-$\alpha,\beta$-unsaturated ketones **74a** and **75a** as the only isolable products. Oxidation of $\beta,\gamma$-unsaturated ketones by Mn(III) to $\gamma$-acetoxy-$\alpha,\beta$-unsaturated ketones is well known.[12]

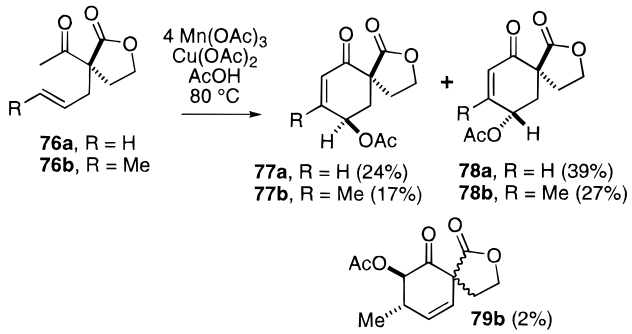
The stereochemistry of **74a** and **75a** was assigned on the basis of the coupling constants of the C*H*OAc proton to the adjacent methylene group, which are 5.4 and 10.0 Hz for **75a** and 5.1 and 7.8 Hz for **74a**. MM2 calculations[11] suggest that this proton should be exclusively axial, with larger coupling constants, in **75a**, in which the acetate and the larger, methyl group are *cis*. In **74a**, with the acetate and smaller, ester group *cis*, both conformers are populated so that this proton is equatorial a significant percentage of the time.[21]

Oxidative cyclization of α-crotylacetoacetate **71b** proceeds similarly, affording 47% of a 2:1 mixture of **74b** and **75b**. The stereochemistry was assigned on the basis of the coupling constants of the C*H*OAc proton to the adjacent methylene group, which are 5.4 and 9.6 Hz for




**75b** and 4.8 and 6.9 Hz for **74b**, as discussed above. These results indicate that oxidative cyclization of ketones may be useful even when enolization and subsequent oxidation of the initial product occur since $\gamma$-acetoxy-$\alpha,\beta$-unsaturated ketones are obtained in good yield.

Similar results are obtained with 2-acetyl-2-allylbutyrolactone (**76a**), which affords 39% of **78a** and 24% of **77a**, and with 2-acetyl-2-crotylbutyrolactone (**76b**), which affords 27% of **78b**, 17% of **77b**, and 2% of **79b**. The stereochemical assignments of **77** and **78** follow from the coupling constants of the C*H*OAc proton to the adjacent methylene group, which are 5.3 and 10.9 Hz for **78a**, 5.2 and 10.8 Hz for **78b**, and 5.4 and 8.2 Hz for **77a**.



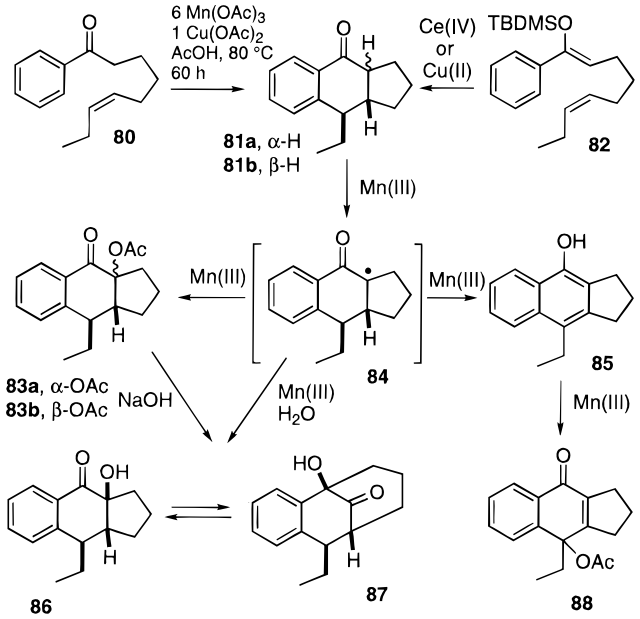

**Oxidative Cyclization of 1-Phenyl-6-nonen-1-one (80).** Several years ago we reported that oxidative cyclization of silyl enol ether **82** with either Ce(IV) or Cu(II) provides tricyclic ketones **81a,b** in excellent yield.[22] These reactions proceed via cation radicals rather than radicals and provide **81a,b** in excellent yield because the silyl enol ether **82** is more easily oxidized than the product ketone **81a,b**. We examined the oxidative cyclization of ketone **80** to determine whether the expected initial product, tricyclic ketone **81a,b**, is stable to the conditions required for Mn(III) oxidation of **80**. Oxidative cyclization of **80** with 6 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in AcOH for 60 h at 80 °C provides 15% of **83a**, 9% of **83b**, 9% of **88**, and none of **81a,b**. Apparently, oxidation of **81a,b** to radical **84** is faster than oxidation of **80**. Further oxidation of radical **84** will provide acetates **83a,b** and phenol **85**, which is oxidized to acetoxy enone **88**.[23] The structures of **83a,b** were assigned on the basis of the similarity of the proton and carbon NMR spectra to those of **81a,b**.

We established that tricyclic ketones **81a,b** are competent intermediates by treating **81a,b**[22] with 2 equiv of

(21) The observed coupling constants are similar to those observed for related 4-acetoxy-2-cyclohexenones: Widmer, E.; Zell, R.; Lukac, T.; Casadei, M.; Schonholzer, P.; Broger, E. A. *Helv. Chim. Acta* **1981**, *64*, 2405.

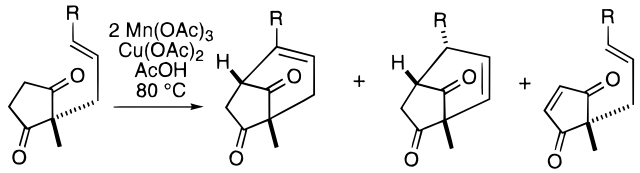
(22) Snider, B. B.; Kwon, T. *J. Org. Chem.* **1992**, *57*, 2399.

(23) For related oxidations of phenols see: Greenland, H.; Pinhey, J. T.; Sternhell, S. *Aust. J. Chem.* **1986**, *39*, 2067; **1987**, *40*, 325.

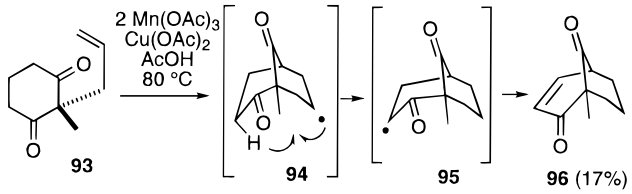



$Mn(OAc)_3$ and 1 equiv of $Cu(OAc)_2$ in AcOH at 80 °C for 48 h to afford 11% of **83a**, 9% of **83b**, 13% of **88**, and 31% of a 3:2 mixture of **86** and **87**. α-Ketol **86** could be formed by oxidation of radical **84** and reaction with water rather than acetate or by hydrolysis of **83b**. Hydrolysis of **83b** with NaOH in EtOH affords 82% of a 1:1 mixture of **86** and **87**. The bridged ketol **87** is formed from the fused ketol **86** by the α-ketol rearrangement.[24]

**Oxidative Cyclization of 2-Allylic-1,3-cycloalkanediones.** Oxidative cyclization of 2-allyl-2-methylcyclopentane-1,3-dione (**89a**) in AcOH at 80 °C for 2 h provides 75% of **90a**, 9% of **91a**, and 2% of enedione **92a**. Similarly, 2-crotyl-2-methylcyclopentane-1,3-dione (**89b**) provides 33% of **90b**,[25] 23% of **91b**, and 6% of enedione **92b**. Although bicyclo[3.2.1]octenediones **90** and **91** could enolize and be oxidized further, they are apparently less acidic than the starting dione **89** and do not react further. Thus, while **71** gives only acetoxy enones **74** and **75** resulting from further oxidation of the initial product **72**, in some cases it is possible to isolate products that can enolize. Oxidative cyclization of **89a** at 80 °C provides a much higher yield of **90a** and **90b** than oxidative cyclization of 4-allyl-2-methylcyclohexanone at 25 °C for 24 h, which gives the same bicyclic radical, but provides only 38% of **90a**.[26]




Oxidative cyclization of cyclohexanedione **93** affords 17% of conjugated cyclohexenone **96** as the only isolable product. Apparently, the initially formed bicyclic radical **94** undergoes a facile transannular 1,5-hydrogen shift[15] to give the more stable α-keto radical **95**. Oxidation of α-keto radicals by either Cu(II) or Mn(III) is inefficient[17] so that cyclohexenone **96** is obtained in low yield.




**Cyclization of 6-Heptenyl and 7-Octenyl Radicals. Oxidative Cyclizations of 97a−c.** The oxidative cyclizations of **97a−c**, **102a−c**, **105a,b**, and **111** were carried out to establish whether medium-sized rings could be obtained from oxidative cyclization of ketones. Treatment of **97a** with 2.5 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in AcOH for 2.5 h at 80 °C provides 7-*endo*-cyclization products **98a** (25%) and **99a** (10%) and 6-*exo*-cyclization product **100a** (25%) and lactone **101a** (12%), which results from a Baeyer−Villiger-type oxidation of **100a**. Thus, the monocyclic α-keto radical obtained from **97a** undergoes 6-*exo*- and 7-*endo*-cyclization in approximately equal amounts.

We were surprised to isolate lactone **101a**, which is much more polar than ketone **100a**. Ketone **100a** displays carbonyl signals at $\delta$ 210.1 and 171.2 in the $^{13}C$ NMR spectrum and absorptions at 1742 and 1712 $cm^{-1}$ in the IR spectrum, whereas lactone **101a** exhibits signals at $\delta$ 171.6 and 170.9 in the $^{13}C$ NMR spectrum and absorptions at 1770 and 1732 $cm^{-1}$ in the IR spectrum, indicating the presence of a $\gamma$-lactone in addition to the ethyl ester. We determined that lactone **101a** is formed by a Baeyer−Villiger oxidation by treating ketone **100a** with 2 equiv of $Mn(OAc)_3 \cdot 2H_2O$ in AcOH for 24 h to provide a 1:1 mixture of **100a** and **101a**.

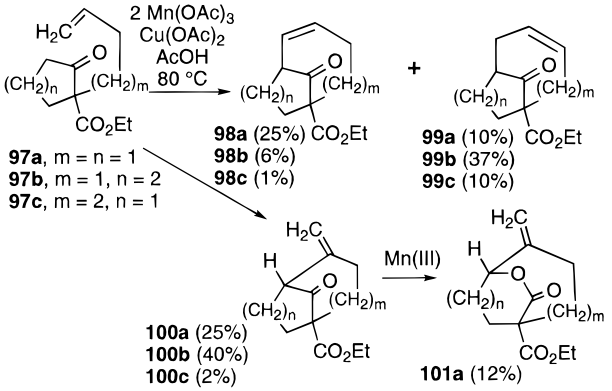
At first we were puzzled as to why **100a** is oxidized to a lactone while **98a**, **99a**, and all previously reported ketones are not, except for **46**, which has a tertiary alkyl group that migrates more readily. An allyl group migrates readily in a Baeyer−Villiger oxidation if the torsion angle between the double bond and the migrating bond is ≈90°, so that the double bond stabilizes the migrating substituent. Examination of models suggests that Baeyer−Villiger reaction of **100a** occurs readily because the torsion angle $H_2C{=}CCHC$ in the stable conformer with a chair cyclohexanone is 118°, which is close to optimal. Baeyer−Villiger reaction of endocyclic analogues **8** and **98a** should be slower since the torsion angle CH=CCHC is 29° and 6°, respectively, which is far from the optimal 90° for migration of an allylic group. Baeyer−Villiger reaction of exocyclic homologue **100b** is slow since the cyclohexanone is calculated to be more stable in the boat conformer with a $H_2C{=}CCHC$ torsion angle of 21°. Other examples of Baeyer−Villiger oxidation of bridged bicyclic ketones are known.[27]

Oxidative cyclization of cyclohexanone **97b** affords 7-*endo*-cyclization products **98b** (6%) and **99b** (37%)[26] and 6-*exo*-cyclization product **100b** (40%). We were surprised to discover that the Cu(II)-mediated oxidative elimination of the cycloheptyl radicals obtained from **97a** and **97b** proceeds with opposite regioselectivity. Cu(II) oxidation affords $\beta,\gamma$-unsaturated cycloheptanone **98a** as the major product from cyclopentanone **97a** but $\gamma,\delta$-unsaturated

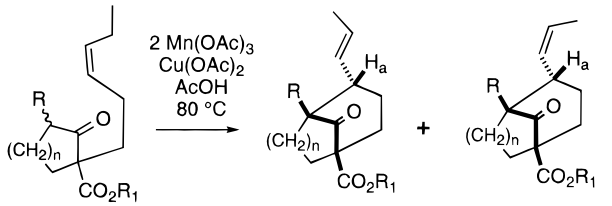
(24) For related α-ketol rearrangements see: Grunewald, G. L.; Walters, D. E.; Kroboth, T. R. *J. Org. Chem.* **1978**, *43*, 3478.
(25) Kasturi, T. R.; Reddy, S. M. *Ind. J. Chem.* **1982**, *21b*, 901.
(26) Kates, S. A.; Dombroski, M. A.; Snider, B. B. *J. Org. Chem.* **1990**, *55*, 2427.
(27) Krow, G. R. *Tetrahedron* **1981**, *37*, 2697. Mehta, G.; Pandey, P. N.; Ho, T.-L. *J. Org. Chem.* **1976**, *41*, 953. Miura, H.; Hirao, K.-I.; Yonemitsu, O. *Tetrahedron* **1978**, *34*, 1805.

cycloheptanone **99b** as the major product from cyclohexanone **97b**.

We were disappointed to find that oxidative cyclization of bishomoallylic cyclopentanone **97c** affords only 1% of **98c**, 10% of **99c**, and 2% of **100c**. Neither 8-*endo*- nor 7-*exo*-cyclization is an efficient process.

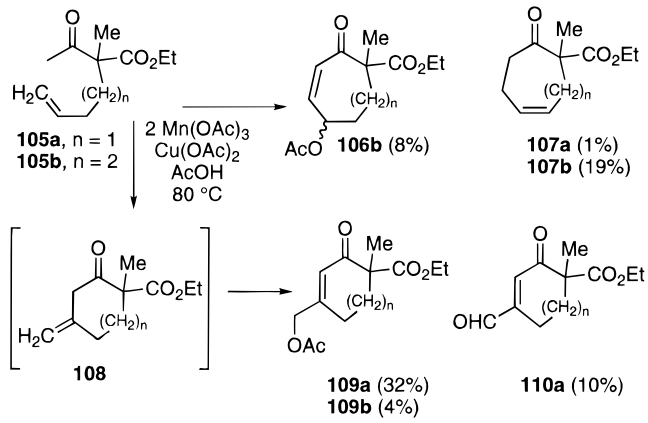



Oxidative cyclization of 3(*Z*)-hexenylcyclopentanone **102a** affords 72% of a 5:2 mixture of 6-*exo*-cyclization products **103a** and **104a**. Similarly, cyclohexanone **102b** provides 66% (75% based on recovered **102b**) of a similar mixture of **103b** and **104b**. The stereochemistry of **103a** follows from the coupling of the allylic methine $H_a$ at $\delta$ 2.70 to the adjacent methylene group with $J = 10.6$ and 6.3 Hz, which establishes that the hydrogen is axial and the propenyl side chain equatorial. The spectral data of the minor isomer **104a** are very similar except for the changes expected for a *Z*-double bond. Cyclization to the 1,2-disubstituted double bond occurs exclusively 6-*exo* through a chair transition state with an equatorial alkenyl group. Surprisingly, Cu(II) oxidation affords a 5:2 *E*/*Z* mixture of double bonds, while closely related examples with an ester at the bridgehead give exclusively the *E*-double bond.[26] We therefore examined the cyclization of the α′-methyl analogue **102c**, which provides 72% of an 8:1 mixture of **103c** and **104c** with much better selectively for the *E*-isomer, indicating that the stereochemistry of the oxidative elimination of radicals to alkenes by $Cu(OAc)_2$ is very sensitive to the local steric environment.

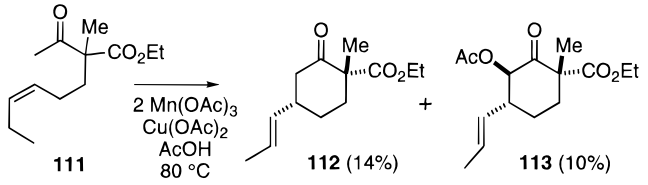



Oxidative cyclization of acetoacetate **105a** yields 7-*endo*-cyclization product **107a** (1%) and 6-*exo*-cyclization products **109a** (32%) and **110a** (10%), which are both derived from further oxidation of β,γ-unsaturated ketone **108a**. Thus, 6-*exo*-cyclization of the acyclic α-keto radical is the predominant process. Oxidative cyclization of **105b** provides 8-*endo*-cyclization products **106b** (8%) and **107b** (19%) and 7-*exo*-cyclization product **109b** (4%).

Oxidative cyclization of **111** proceeds stereospecifically, but in modest yield, giving 14% of cyclohexanone **112** and 10% of acetoxycyclohexanone **113**, which is formed by




further oxidation of **112**. γ,δ-Unsaturated cyclohexanone **112** is oxidized at about the same rate as the starting ketone **111**. The stereochemistry of **112** was assigned based on the chemical shift of the methyl group at $\delta$ 1.27, which corresponds closely to that reported for an equatorial methyl group ($\delta$ 1.28) but not an axial methyl group ($\delta$ 1.45) in an analogous system.[28]



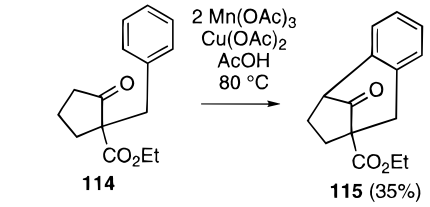

Oxidative cyclization of benzyl cyclopentanone **114** affords 35% of **115**, indicating that α-keto radicals generated by this procedure cyclize onto aromatic rings. Oxidation of the α-keto radical formed from **114** gives 10% of the enone analogous to **6** and 39% of the α-acetoxycyclopentanone analogous to **7**, indicating that, as expected,[29] cyclization of the phenylbutyl radical obtained from **115** is much slower than cyclization of 5-hexenyl radical **3**. Attempted oxidative cyclization of β-keto ester **116** gives none of the desired product **117**. This suggests that α-keto radicals are more reactive than radicals obtained from β-dicarbonyl compounds, which are stabilized by two adjacent carbonyl groups.

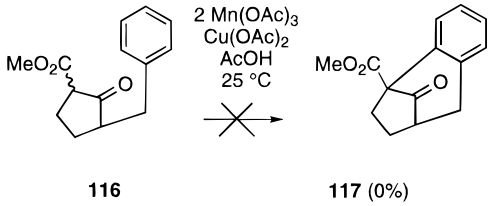
**Tandem Cyclizations.** The selective conversion of acetoacetate **118** to either propenylcyclohexanone **119** or vinylnorbornanone **123** at different temperatures clearly illustrates the difference in reactivity between 1,3-dicarbonyl compounds and ketones. We have previously reported the oxidative cyclization of **118** at 25 °C to give **119** (56%), **120** (3%), and **121** (14%); no **123** is obtained at room temperature.[1a,26] On the other hand, oxidation of **118** with 4 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ for 56 h at 60 °C or 16 h at 80 °C provides 45% of a 1:9 mixture of **122** and **123**, only 10% of **119**, 4% of a 1:2 mixture of **120** and **121**, and a trace of bicycle

(28) Sugai, T.; Kakeya, H.; Ohta, H.; Morooka, M.; Ohba, S. *Tetrahedron* **1989**, *19*, 6135.

(29) Reaction of the 4-phenylbutyl radical with 0.025 M $Cu(OAc)_2 \cdot H_2O$ gives 10% of cyclized product and 86% of oxidized product.[30a] Therefore, $0.025(k_{ox}/k_{r1}) = 86/10 = 8.6$ or $k_{ox}/k_{r1} = 8.6/0.025 = 344$. Reaction of the 5-hexenyl radical with 0.02 M $Cu(OAc)_2 \cdot H_2O$ gives 84% of cyclized product and 9.5% of oxidized product.[30b] Therefore, $0.02 \times k_{ox}/k_{r2} = 9.5/84 = 0.113$ or $k_{ox}/k_{r2} = 0.113/0.02 = 5.65$. Therefore, $k_{r2}/k_{r1} = 344/5.65 = 60.8$ so that cyclization of a 5-hexenyl radical is about 60 times faster than cyclization of a 4-phenylbutyl radical.

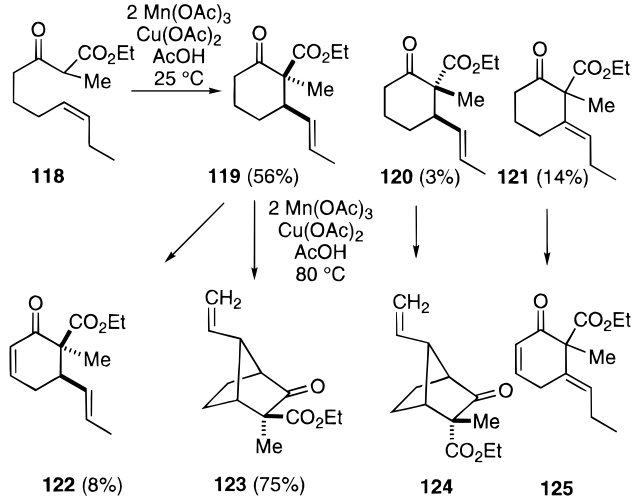
(30) (a) Kochi, J. K.; Gilliom, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 5251. (b) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843.



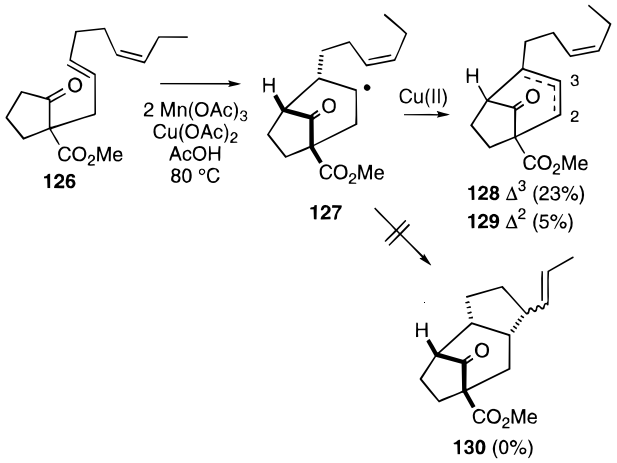

**124** derived from oxidative cyclization of **122**. Oxidation of pure **119** under these conditions provides 75% of **123** and 8% of enone **122**, while oxidation of the 1:2 mixture of **120** and **121** with 2 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of $Cu(OAc)_2 \cdot H_2O$ in AcOH at 80 °C for 16 h affords 70% of a 1:2 mixture of **124** and **125**.

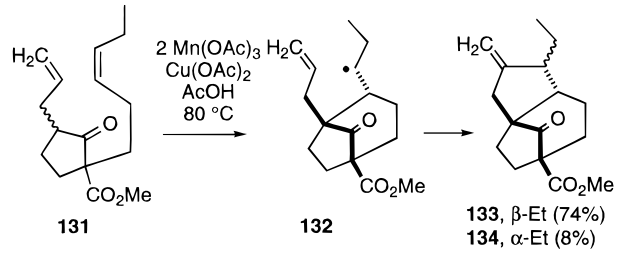
At elevated temperatures cyclohexanone **119** is oxidized to the α-keto radical, which undergoes a 5-*exo*-cyclization stereospecifically to give the less hindered secondary radical, which is oxidized by Cu(II) to afford **123** with the less substituted double bond.[5] Decoupling established that the allylic hydrogen of **123** at $\delta$ 2.88 was weakly coupled to the *endo* hydrogens at $\delta$ 1.70 and 1.48, but not the *exo* hydrogens at $\delta$ 2.06 and 1.76. A long-range coupling between the allylic methine and the *endo* hydrogens requires a W relationship, which is only possible for the anti isomer **123**.




Attempted tandem cyclization of **126** was unsuccessful, giving only the bicyclic products **128** (23%) and **129** (5%), which are formed analogously to **8e** and **9e**, and none of the desired tricyclic product **130**. Apparently, oxidation of bicyclic radical **127** is faster than the second cyclization. No **130** was obtained even when the reaction was repeated with 2 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and only a catalytic amount (5 mol%) of $Cu(OAc)_2 \cdot H_2O$ to slow down the oxidation of radical **127**. This suggests that cyclization of bicyclic radical **127**, which would have to occur on the sterically hindered endo face, is very slow.

Tandem oxidative cyclization of **131** affords 82% of a 9:1 mixture of tricyclic ketones **133** and **134**. Oxidation and 6-*exo*-cyclization affords bicyclic radical **132** stereospecifically as previously discussed in the cyclization of **102c**. A second, 5-*exo*-cyclization followed by oxidation of the resulting primary radical affords **133** and **134**. The stereochemistry of the ethyl group is tentatively assigned on the basis of MM2 calculations[11] that suggest **133** is less strained.




**Conclusion.** These results vastly extend the scope of Mn(III)-based oxidative cyclizations beyond 1,3-dicarbonyl compounds. A wide variety of unsaturated ketones can now be used as substrates. The formation of **57a** suggests that kinetically controlled enolization is the rate-determining step in α-keto radical formation. Bridged bicyclic ketones that cannot enolize further are isolated in good yield. $\beta,\gamma$-Unsaturated monocyclic ketones that can enolize are oxidized to $\gamma$-acetoxy enones.

## Experimental Section

**General Procedures.** $^1$H NMR spectra were recorded at 300 MHz in $CDCl_3$. Chemical shifts are reported in $\delta$ and coupling constants in Hz. IR spectra are reported in $cm^{-1}$. All air-sensitive reactions were run under $N_2$ in flame-dried glassware with magnetic stirring.

**Oxidative Cyclization of Ethyl 2-Oxo-1-(2-propenyl)-cyclopentanecarboxylate (1a).** A solution of $\beta$-keto ester **1a** (98 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (303 mg, 1.125 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 5 mL of degassed AcOH was stirred under $N_2$ for 1.5 h at 80 °C. The mixture was diluted with water (20 mL), and a 10% solution of $NaHSO_3$ was added dropwise until all residual Mn(III) was reduced to Mn(II). The resulting solution was extracted with three 20 mL portions of $CH_2Cl_2$. The combined extracts were washed with saturated $NaHCO_3$ and brine solutions. The solvent was removed under reduced pressure to yield 96 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) gave 74 mg of an 8:1 mixture of **8a** and **9a**, followed by 15 mg of a 10:5:1 mixture of **8a**, **9a**, and **6a** and 6 mg of polymeric material. The calculated yields are ≤1% of **6a**, 75% of **8a**, and 15% of **9a**.

A trace of enone **6a** was observed in the $^1$H NMR spectrum of the mixture: 7.75 (ddd, 1, $J$ = 2.4, 2.4, 5.7), 6.16 (br d, 1, $J$ = 5.7).

The data for **8a**: $^1$H NMR 5.84 (dddd, 1, $J$ = 9.3, 6.7, 2.5, 0.8), 5.62 (ddd, 1, $J$ = 9.3, 4.0, 2.5), 4.23 (q, 2, $J$ = 7.2), 3.30 (dddd, 1, $J$ = 17.7, 2.5, 2.5, 2.5), 2.69 (br dd, 1, $J$ = 17.7, 4.0), 2.69−2.62 (m, 2), 2.14−2.09 (m, 3), 1.29 (t, 3, $J$ = 7.2); $^{13}$C NMR 211.1, 171.2, 131.7, 125.5, 61.3, 55.8, 46.3, 44.7, 30.9, 28.9, 14.2; IR (neat) 1759, 1728. The data are identical to those previous reported.[3]

The data for **9a** were obtained from the mixture: $^1$H NMR 6.10 (br dd, 1, $J$ = 9.1, 2.4), 5.65−5.69 (m, 1), 4.25 (q, 2, $J$ = 7.1), 2.95 (br d, 1, $J$ = 17.0), 2.61−2.49 (m, 3), 2.37 (ddd, 1, $J$ = 12.8, 10.3, 2.5), 2.28−2.14 (m, 1), 1.84−1.73 (m, 1), 1.29 (t, 3, $J$ = 7.1); $^{13}$C NMR (partial) 132.0, 125.4, 61.4, 43.3, 42.4, 29.7, 14.2.

**Oxidative Cyclization of Ethyl 2-Oxo-1-(2-propenyl)-cyclohexanecarboxylate (1b).** Reaction of $\beta$-keto ester **1b** (105 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (303 mg, 1.125 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 5 mL of degassed AcOH for 16 h at 80 °C followed by normal workup gave 99 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 1 mg (<1%) of recovered **1b**, followed by 4 mg (4%) of **10b**, 66 mg (63%) of **8b**, and 7 mg (7%) of **9b**.

The data for **8b**: $^1$H NMR 5.96 (dt, 1, $J$ = 9.6, 3.5), 5.58 (dddd, 1, $J$ = 9.6, 6.0, 2.4, 1.5), 4.23 (q, 2, $J$ = 7.2), 3.37 (br d, 1, $J$ = 18.6), 2.95−2.91 (m, 1), 2.56 (ddd, 1, $J$ = 18.6, 3.5, 1.5), 2.38−2.32 (m, 1), 2.07−1.92 (m, 4), 1.69−1.63 (m, 1), 1.29 (t, 3, $J$ = 7.2); $^{13}$C NMR 210.3, 171.9, 128.9, 126.1, 61.3, 58.4, 47.4, 39.2, 38.9, 32.9, 17.1, 14.1; IR (neat) 1738, 1716. The data are identical to those previously reported.[6,7]

The data for **9b**: $^1$H NMR 6.06 (br dt, 1, $J$ = 9.7, 3.2), 5.66 (ddd, 1, $J$ = 9.7, 2.6, 1.3), 4.25 (q, 2, $J$ = 7.2), 2.82 (dddd, 1, $J$ = 18.6, 7.2, 3.2, 2.6), 2.68−2.65 (m, 1), 2.46 (ddd, 1, $J$ = 18.6, 3.2, 1.3), 2.40−2.28 (m, 1), 2.05−1.86 (m, 4), 1.17−1.65 (m, 1) 1.28 (t, 3, $J$ = 7.2); IR (neat) 1741, 1714. The data are identical to those previously reported.[6]

The data for **10b**: $^1$H NMR 5.05 (br s, 2), 4.22 (q, 2, $J$ = 7.1), 3.29 (br dd, 1, $J$ = 17.3, 1.2), 2.98−2.96 (m, 1), 2.73 (br dd, 1, $J$ = 17.3, 1.1), 2.36 (dddd, 1, $J$ = 15.1, 12.3, 5.5, 1.5), 2.20−1.97 (m, 3), 1.94−1.76 (m, 1), 1.68−1.61 (m, 1), 1.26 (t, 3, $J$ = 7.1). The data are identical to those previously reported.[8]

**Oxidative Cyclization of Methyl 2-Oxo-1-(2-propenyl)-cycloheptanecarboxylate (1c).** $Mn(OAc)_3 \cdot 2H_2O$ (1.333 g, 4.97 mmol), $Cu(OAc)_2$ (225 mg, 1.24 mmol), and **1c** (261 mg, 1.24 mmol) were stirred in 12 mL of glacial acetic acid at 80 °C for 85 h. Normal workup and flash chromatography of the residue on silica gel (10:1 hexane/EtOAc, 2:1:0.2 hexane/EtOAc/$CH_2Cl_2$) gave 50 mg (19%) of unreacted **1c**, followed by 36 mg of a 1:5 mixture of **1c** and **10c**, 79 mg of a 1:2 mixture of **10c** and **8c**, and 4 mg of a 1:3:7 mixture of **10c**, **8c**, and **9c**. The calculated yields of **8c**, **9c**, and **10c** are 21%, 1%, and 22%, respectively.

The data for **8c**: $^1$H NMR 5.84 (br dd, 1, $J$ = 9.8, 6.0), 5.66 (br dd, 1, $J$ = 9.8, 2.8), 3.78 (s, 3), 3.06 (m, 2), 2.50 (br dd, 1, $J$ = 13.9, 6.6), 2.39 (ddd, 1, $J$ = 17.0, 6.0, 1.0), 1.90−1.32 (m, 6), 1.22 (m, 1); $^{13}$C NMR 212.0, 172.3, 129.1, 125.9, 61.5, 52.3, 50.7, 37.0, 33.3, 31.5, 27.4, 26.1; IR (neat) 1738, 1716. Anal. Calcd for $C_{12}H_{16}O_3$ (for the 2:1 mixture of **8c** and **10c**): C, 69.21; H, 7.74. Found: C, 69.37; H, 7.91.

The data for **9c**: $^1$H NMR 6.04 (br dd, 1, $J$ = 9.8, 6.1), 5.57 (dd, 1, $J$ = 9.8, 2.9), 3.68 (s, 3), 2.88 (br ddd, 1, $J$ = 10.7, 4.9, 4.2), 2.70 (dddd, 1, $J$ = 17.5, 4.9, 2.9, 2.4), 2.30 (ddd, 1, $J$ = 17.5, 6.1, 1.7), 2.16 (m, 2), 2.00−1.40 (m, 4), 1.13 (m, 2); $^{13}$C NMR 210.2, 172.0, 128.5, 128.4, 62.2, 52.5, 46.2, 34.0, 33.2, 30.3, 25.9, 25.2; IR (neat) 1742, 1710.

The data for **10c**: $^1$H NMR 5.12 (br s, 1), 5.06 (br s, 1), 3.76 (s, 3), 3.42 (br d, 1, $J$ = 17.2), 3.14 (m, 1), 2.64 (dddd, 1, $J$ = 17.2, 2, 2, 2), 2.16−1.97 (m, 2), 1.85−1.54 (m, 4), 1.39 (m, 2); $^{13}$C NMR 213.5, 172.5, 147.7, 109.2, 61.5, 52.6, 51.5, 40.5, 34.5, 31.3, 25.0, 23.1; IR (neat) 1755, 1732.

**Oxidative Cyclization of Ethyl 2-Oxo-1-(2-propenyl)-cyclooctanecarboxylate (1d).** $Mn(OAc)_3 \cdot 2H_2O$ (2.03 g, 7.56 mmol), $Cu(OAc)_2$ (171 mg, 0.95 mmol), and **1d** (226 mg, 0.95 mmol) were stirred in 20 mL of glacial acetic acid at 80 °C for 226 h. Normal workup and flash chromatography of the residue on silica gel (15:1 hexane/EtOAc, 2:1:0.2 hexane/EtOAc/$CH_2Cl_2$) gave 22 mg (10%) of unreacted **1d**, followed by 172 mg (62%) of **11d**: $^1$H NMR 6.32 (d, 1, $J$ = 4.8), 5.56 (dddd, 1, $J$ = 6.5, 6.3, 4.8, 1.0), 4.24 (q, 2, $J$ = 7.1), 2.77 (ddd, 1, $J$ = 12.9, 5.5, 5.5), 2.61 (dd, 1, $J$ = 14.6, 6.3), 2.40 (ddd, 1, $J$ = 14.6, 6.5, 0.8), 2.34 (ddd, 1, $J$ = 15.7, 8.8, 1.1), 2.06 (s, 3), 1.99 (m, 1), 1.79−1.51 (m, 6), 1.30 (t, 3, $J$ = 7.1), 1.23 (m, 1); $^{13}$C NMR 201.6, 171.5, 170.7, 145.9, 132.5, 66.4, 61.2, 58.7, 38.4, 35.2, 30.7, 29.2, 27.6, 26.2, 21.0, 14.1; IR (neat) 1736, 1702; UV (EtOH) $\lambda_{max}$ 231.1 nm ($\epsilon$ 6667). Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.54. Found: C, 65.69; H, 7.50.

**Oxidative Cyclization of Ethyl 1-(2(*E*)-Butenyl)-2-oxocyclopentanecarboxylate (1e).** Reaction of **1e** (105 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (304 mg, 1.125 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 10 mL of degassed AcOH at 80 °C for 1.5 h followed by normal workup gave 101 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 75 mg (75%) of a 10:1 mixture of **8e** and **9e**, followed by 11 mg (11%) of a 2:1 mixture of **8e** and **9e**, 1 mg (1%) of enone **6e**, and 3 mg (2%) of acetate **7e**. The calculated yields are <1% of enone **6e**, 2% of acetate **7e**, 73% of **8e**, and 10% of **9e**.

The $^1$H NMR data for **6e**: $^1$H NMR 7.77−7.31 (m, 1), 6.19−6.13 (m, 1), 5.58−5.50 (m, 2), 4.17 (q, 2, $J$ = 7.1), 3.24−3.14 (m, 1), 2.69−2.54 (m, 3), 1.64−1.61 (m, 3), 1.24 (t, 3, $J$ = 7.1).

The data for **8e**: $^1$H NMR 5.28 (m, 1), 4.22 (q, 2, $J$ = 7.1), 3.18 (dd, 1, $J$ = 17.1, 2.2), 2.66−2.63 (m, 1), 2.56 (ddd, 1, $J$ = 17.1, 3.7, 2.0), 2.45−2.42 (m, 1), 2.13−2.05 (m, 3), 1.74 (d, 3, $J$ = 1.5), 1.28 (t, 3, $J$ = 7.1); $^{13}$C NMR 211.4, 171.4, 140.2, 118.3, 61.3, 55.1, 50.9, 42.9, 30.8, 27.9, 22.0, 14.2; IR (neat) 1760, 1727. The data are identical to those previously reported.[13]

Partial $^1$H NMR data for **9e** were obtained from the 2:1 mixture of **8e** and **9e**: 6.01 (dd, 1, $J$ = 9.3, 2.6), 5.45 (ddd, 1, $J$ = 9.3, 2.1, 1.2), 4.24 (q, 2, $J$ = 7.1), 1.29 (t, 3, $J$ = 7.1), 1.10 (d, 3, $J$ = 7.2).

**Oxidative Cyclization of Ethyl 1-(2(*Z*)-butenyl)-2-oxocyclopentanecarboxylate (1f).** Reaction of **1f** (105 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (402 mg, 1.5 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 10 mL of degassed AcOH at 80 °C for 2 h followed by normal workup gave 112 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 13 mg (13%) of **8f** = **8e**, followed by 4 mg (4%) of enone **6f**, 8 mg (6%) of a 1:1 mixture of acetates **7f**, and 65 mg (65% by weight) of polymeric material.

The data for **6f**: $^1$H NMR 7.76 (dt, 1, $J$ = 5.7, 2.7), 6.17 (dt, 1, $J$ = 5.7, 2.7), 5.59 (dddq, 1, $J$ = 8.4, 1.2, 1.2, 6.9), 5.21 (ddt, 1, $J$ = 8.4, 1.4, 7.2), 4.16 (q, 2, $J$ = 7.1), 3.02 (br dt, 1, $J$ = 19.3, 2.5), 2.78 (br dd, 1, $J$ = 14.4, 7.2), 2.60 (ddd, 1, $J$ = 19.3, 2.7, 2.2), 2.54 (br dd, 1, $J$ = 14.4, 7.2), 1.63 (d, 3, $J$ = 6.9), 1.24 (t, 3, $J$ = 7.1).

The $^1$H NMR data for acetates **7f** were determined from the 1:1 mixture: 5.71−5.60 (m, 1), 5.38−5.30 (m, 1), 5.34 (dd, 0.5 × 1, $J$ = 11.5, 8.7), 5.08 (dd, 0.5 × 1, $J$ = 11.5, 8.5), 4.19 (q, 0.5 × 2, $J$ = 7.1), 4.17 (q, 0.5 × 2, $J$ = 7.1), 2.72 (br dd, 0.5 × 1, $J$ = 13.2, 7.2), 2.70 (br dd, 0.5 × 1, $J$ = 13.2, 7.2), 2.56−2.35 (m, 2), 2.15 (s, 0.5 × 3), 2.14 (s, 0.5 × 3), 2.14−1.95 (m, 2), 1.88−1.70 (m, 0.5), 1.67−1.62 (m, 0.5), 1.66 (d, 0.5 × 3, $J$ = 6.9), 1.62 (d, 0.5 × 3, $J$ = 6.9), 1.25 (t, 0.5 × 3, $J$ = 7.1), 1.27 (t, 0.5 × 3, $J$ = 7.1).

A trace of **9f** (<1%) was observed in the crude mixture of products: $^1$H NMR 6.05 (d, 1, $J$ = 9.9), 1.11 (d, 3, $J$ = 7.1).

**Oxidative Cyclization of Ethyl 1-(2(*E*)-Butenyl)-2-oxocyclohexanecarboxylate (12a).** Reaction of **12a** (112 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (335 mg, 1.25 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 10 mL of degassed AcOH at 80 °C for 16 h followed by normal workup gave 107 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 38 mg (35%) of a 1:1:5:2 mixture of **16**, **18**, **20**, and **24a**, followed by 42 mg (38%) of a 5.6:3.2:7:2:1:2 mixture of **16**, **18**, **20**, **21a**, **23a**, and **24a** and 8 mg (7%) of a 2:1:3:1 mixture of **16**, **18**, **21a**, and **23a**. The calculated yields of the products are 18% of **16**, 13% of **18**, 32% of **20**, 7% of **21a**, 2% of **23a**, and 7% of **24a**.

Reaction of **12a** (112 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (402 mg, 1.25 mmol), and $Cu(OAc)_2 \cdot H_2O$ (10 mg, 0.05 mmol) in 10 mL of degassed AcOH at 80 °C for 16 h followed by normal workup gave 109 mg of a pale yellow oil. Purification by flash

chromatography (20:1 hexane/EtOAc) afforded 5 mg (4%) of recovered **12a**, followed by 21 mg (19%) of a 5:1 mixture of **24a** and **20**, 27 mg (25%) of a 0.1:2:10:3 mixture of **16**, **18**, **20**, and **24a**, 22 mg (20%) of a 3:1:3 mixture of **16**, **18**, and **20**, 10 mg (9%) of a 3:1:3:3 mixture of **16**, **18**, **21a**, and **23a**, 6 mg (5%) of a 3:1:6:3 mixture of **16**, **18**, **21a**, and **23a**, and 2 mg (2%) of a 1:2:1 mixture of **16**, **21a**, and **23a**. The calculated yields of the products are 15% of **16**, 10% of **18**, 26% of **20**, 6% of **21a**, 5% of **23a**, and 18% of **24a**.

The data for **16**: $^1$H NMR 5.79 (ddd, 1, $J$ = 17.0, 10.1, 8.3), 5.03 (br d, 1, $J$ = 17.0), 4.95 (br d, 1, $J$ = 10.1), 4.23 (q, 2, $J$ = 7.1), 2.66 (ddd, 1, $J$ = 9.1, 8.3, 4.6), 2.42−2.27 (m, 4), 2.25 (ddd, 1, $J$ = 11.7, 5.3, 1.2), 2.15−2.06 (m, 1), 1.92−1.79 (m, 2), 1.75−1.67 (m, 1), 1.28 (t, 3, $J$ = 7.1); $^{13}$C NMR 214.4, 171.1, 141.5, 113.3, 61.2, 58.4, 52.4, 38.8, 38.4, 36.1, 34.5, 18.1, 14.2; IR (neat) 1749, 1728.

Partial $^1$H NMR data for **18** were obtained from the mixture: 6.01 (dddd,1, $J$ = 16.6, 10.1, 6.8, 0.8), 5.40 (br d, 1, $J$ = 16.6), 5.25 (br d, 1, $J$ = 10.1).

Partial $^1$H NMR data for **20** were obtained from the mixture: 5.56 (m, 1), 4.23 (q, 2, $J$ = 7.2), 3.32 (br d, 1, $J$ = 18.4), 2.74−2.69 (m, 1), 2.44−2.40 (m, 1), 1.29 (t, 3, $J$ = 7.2). The data are identical to those previously reported.[14]

Partial $^1$H NMR data for **21a** were obtained from the mixture: 5.89 (ddd, 1, $J$ = 9.7, 2.3, 0.8), 5.58 (ddd, 1, $J$ = 9.7, 2.7, 1), 4.25 (q, 2, $J$ = 7.2), 2.99−2.90 (m, 1), 2.45−2.54 (m, 1), 1.30 (t, 3, $J$ = 7.2); 1.16 (d, 3, $J$ = 7.5).

Partial $^1$H NMR data for **23a** were obtained from the mixture: 6.00 (dt, 1, $J$ = 9.8, 3.6), 5.64 (ddd, 1, $J$ = 9.8, 2.2, 1.5), 4.22 (q, 2, $J$ = 7.1), 3.65 (br d, 1, $J$ = 17.7), 1.30 (t, 3, $J$ = 7.1), 1.02 (d, 3, $J$ = 6.8).

Partial $^1$H NMR data for **24a** were obtained from the mixture: 5.98 (ddd, 1, $J$ = 9.8, 3.3, 3.3), 5.60 (m, 1), 4.23 (q, 2, $J$ = 7.2), 3.41 (br d, 1, $J$ = 18.8), 2.78 (dd, 1, $J$ = 5.8, 3.6), 2.51 (ddd, 1, $J$ = 18.8, 3.4, 1.8), 2.34 (dddd, 1, $J$ = 13.6, 13.6, 5.3, 1.8), 2.16−2.04 (m, 1), 1.90−2.00 (m, 2), 1.76−1.56 (m, 1), 1.29 (t, 3, $J$ = 7.2), 0.95 (d, 3, $J$ = 6.8).

**Oxidative Cyclization of Ethyl 1-(2(*Z*)-Butenyl)-2-oxocyclohexanecarboxylate (12b).** Reaction of **12b** (112 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (335 mg, 1.25 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 10 mL of degassed AcOH at 80 °C for 16 h followed by normal workup gave 108 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 3 mg (3%) of a 1:4 mixture of **24b** and **17**, followed by 5 mg (4%) of a 1:3:3:2 mixture of **16**, **18**, **20**, and **24b**, 43 mg (40%) of a 12:1 mixture of **16** and **18**, 4 mg (3%) of a 7:1:2:1 mixture of **16**, **18**, **21b**, and **23b**, and 6 mg (5%) of a 5:1 mixture of **18** and **21b**. The calculated yields of the products are 46% of **16**, <1% of **17**, 5% of **18**, 2% of **20**, 2% of **21b**, 1% of **23b** and 2% of **24b**.

Partial $^1$H NMR data for **17** were obtained from the mixture: 5.50−5.38 (m, 1), 1.66 (br d, 3, $J$ = 8.8).

Partial $^1$H NMR data for **21b** were obtained from the mixture: 6.02−5.98 (m, 1), 5.61 (dd, 1, $J$ = 9.6, 1.2), 1.07 (d, 3, $J$ = 7.2).

Partial $^1$H NMR data for **23b** were obtained from the mixture: 5.98−5.94 (m, 1), 5.68−5.63 (m, 1), 1.00 (d, 3, $J$ = 7.3).

Partial $^1$H NMR data for **24b** were obtained from the mixture: 5.90 (dt, 1, $J$ = 9.4, 3.5), 5.68−5.62 (m, 1), 4.23 (q, 2, $J$ = 7.1), 3.42 (br d, 1, $J$ = 17.9), 2.66−2.52 (m, 3), 1.27 (t, 3, $J$ = 7.1), 1.05 (d, 3, $J$ = 7.6).

**Oxidative Cyclization of Ethyl 1-(3-Methyl-2-butenyl)-2-oxocyclopentanecarboxylate (25).** Reaction of **25** (120 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (402 mg, 1.5 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 10 mL of degassed AcOH at 80 °C for 2.5 h followed by normal workup gave 108 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 6 mg (5%) of **26a**, followed by 7 mg (6%) of a 2:1 mixture of **26a** and **28a**, 7 mg (6%) of enone **27a**, and 72 mg of polymeric material.

The data for **26a**: $^1$H NMR 5.93 (d, 1, $J$ = 9.3), 5.39 (dd, 1, $J$ = 9.3, 1.4), 4.25 (q, 2, $J$ = 7.1), 2.53−2.43 (m, 1), 2.17−1.97 (m, 4), 1.30 (t, 3, $J$ = 7.1), 1.12 (br s, 6); $^{13}$C NMR 209.1, 170.5, 136.0, 127.5, 61.3, 54.4, 47.3, 31.9, 27.8, 26.0 (2C), 18.8, 14.2; IR (neat) 1757, 1728. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.91; H, 8.27.

The data for **27a**: $^1$H NMR 7.75 (dt, 1, $J$ = 5.8, 2.7), 6.16 (dt, 1, $J$ = 5.8, 2.2), 4.94 (dt, 1, $J$ = 1.5, 7.8), 4.16 (q, 2, $J$ = 7.1), 3.19 (ddd, 1, $J$ = 19.2, 2.7, 2.2), 2.72 (br dd, 1, $J$ = 14.5, 7.8), 2.59 (ddd, 1, $J$ = 19.2, 2.7, 2.2), 2.47 (br dd, 1, $J$ = 14.5, 7.8), 1.65 (s, 3), 1.63 (s, 3), 1.24 (t, 3, $J$ = 7.1).

Partial $^1$H NMR data for **28a** were obtained from the mixture: 4.75 (br s,1), 4.73 (br s,1), 4.21 (q, 2, $J$ = 7.1), 1.56 (s, 3), 1.25 (t, 3, $J$ = 7.1).

**Oxidative Cyclization of Ethyl 1-(3-Methyl-2-butenyl)-2-oxocyclohexanecarboxylate (25b).** Reaction of $\beta$-keto ester **25b** (112 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (335 mg, 1.25 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 5 mL of degassed AcOH at 80 °C for 18 h followed by normal workup gave 106 mg of a pale yellow crude oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 15 mg (13%) of recovered **25b**, followed by 56 mg (51%) of **28b**.

A trace of **26b** was observed in the $^1$H NMR spectrum of recovered **25b**: $^1$H NMR 5.91 (d, 1, $J$ = 9.8), 1.00 (s, 3), 0.98 (s, 3).

The data for **28b**: $^1$H NMR 4.75 (t, 1, $J$ = 0.9), 4.67 (t, 1, $J$ = 1.5), 4.21 (q, 2, $J$ = 7.1), 2.67 (dd, 1, $J$ = 10.3, 4.4), 2.45 (ddd, 1, $J$ = 14.1, 4.4, 1.4), 2.38−2.22 (m, 3), 2.13 (br dd, 1, $J$ = 13.3, 5.0), 2.06−2.00 (m, 2), 1.94−1.72 (m, 2), 1.69 (d, 3, $J$ = 1.4), 1.28 (t, 3, $J$ = 7.1); $^{13}$C NMR (partial) 171.2, 110.1, 61.1, 58.7, 51.9, 42.5, 38.6, 36.6, 34.1, 19.7, 18.0, 14.1; IR (neat) 1748, 1727.

A trace of **29b** was observed in the $^1$H NMR spectrum of **28b**: 5.11 (br s, 1), 5.01 (br s, 1).

**Oxidative Cyclization of Ethyl 1-(2-Methyl-2-propenyl)-2-oxocyclopentanecarboxylate (30a).** Reaction of **30a** (105 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (302 mg, 1.125 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 5 mL of degassed AcOH at 80 °C for 1.5 h followed by normal workup gave 101 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 26 mg (26%) of a 3:4:1 mixture of **35**, **34**, and **33**, followed by 15 mg (15%) of a 2:1.5:1 mixture of **35**, **34**, and **33**, 9 mg (9%) of a 1:1:2 mixture of **35**, **34**, and **33**, 3 mg (3%) of **44a**, 5 mg (5%) of acetate **36a**, 5 mg (5%) of acetate **37a**, and 5 mg (5%) of **42a**. The calculated yields are 6% of **33a**, 22% of **34a**, 22% of **35a**, 5% of **36a**, 5% of **37a**, 5% of **42a**, and 3% of **44a**. Similar results were obtained from the oxidative cyclization of **30a** with $Mn(OAc)_3 \cdot 2H_2O$ and no $Cu(OAc)_2 \cdot H_2O$.

Partial $^1$H NMR data for **33a** were obtained from the mixture: 5.54 (dt, 1, $J$ = 8.9, 1.7), 4.22 (q, 2, $J$ = 7.2), 3.25 (br d, 1, $J$ = 17.3), 2.58 (d, 1, $J$ = 17.3), 1.69 (br s, 3), 1.29 (t, 3, $J$ = 7.2).

Partial $^1$H NMR data for **34a** were obtained from the mixture: 5.81 (br s, 1), 4.22 (q, 2, $J$ =7.2), 2.89 (br d, 1, $J$ = 16.8), 2.32 (ddd, 1, $J$ = 12.9, 10.2, 2.5), 1.29 (t, 3, $J$ =7.2).

Partial $^1$H NMR data for **35a** were obtained from the mixture: 5.03 (br d, 2, $J$ = 1.9), 4.22 (q, 2, $J$ = 7.1), 3.01 (br d, 1, $J$ = 14.1), 2.73 (br d, 1, $J$ = 14.1), 1.28 (t, 3, $J$ = 7.1).

The data for **36a**: $^1$H NMR 4.21 (q, 2, $J$ = 7.1), 3.01 (br dd, 1, $J$ = 15.2, 4.2), 2.93 (br dt, 1, $J$ = 15.2, 4.1), 2.64−2.52 (m, 1), 2.48 (dd, 1, $J$ = 15.4, 1.5), 2.40−2.28 (m, 2), 2.13 (dd, 1, $J$ = 14.9, 2.8), 2.07 (s, 3), 2.05−1.93 (m, 2), 1.59 (s, 3), 1.28 (t, 3, $J$ = 7.1); $^{13}$C NMR (partial) 170.8, 170.3, 80.2, 61.4, 55.8, 48.3, 45.7, 44.3, 27.2, 26.3, 22.9, 21.0, 14.2; IR (neat) 1760, 1732.

The data for **37a**: $^1$H NMR 4.22 (q, 2, $J$ = 7.1), 3.44 (dt, 1, $J$ = 15.1, 1.9), 2.82 (dddd, 1, $J$ = 15.7, 6.0, 2.3, 1.2), 2.56 (ddd, 1, $J$ = 11.3, 9.8, 1.5), 2.38−2.31 (m, 2), 2.26 (dd, 1, $J$ = 14.7, 1.0), 2.21−1.90 (m, 2), 1.93 (s, 3), 1.83−1.69 (m, 1), 1.69 (s, 3), 1.29 (t, 3, $J$ = 7.1); $^{13}$C NMR 211.3, 170.9, 170.1, 77.7, 61.4, 53.8, 49.3, 48.5, 40.5, 28.9, 26.5, 24.1, 22.4, 14.2; IR (neat) 1755, 1732. Anal. Calcd for $C_{14}H_{20}O_5$ (1:1 mixture of acetates **36a** and **37a**): C, 62.67; H, 7.51. Found: C, 62.65; H, 7.29.

The data for **42a**: $^1$H NMR 6.91 (d, 1, $J$ = 2.4), 4.21 (q, 2, $J$ = 7.1), 3.05 (dt, 1, $J$ = 2.4, 6.9), 2.92 (dt, 1, J = 17.1, 4.4), 2.56 (dddd, 1, $J$ = 17.7, 12.2, 4.2, 2.4), 2.33−2.17 (m, 3), 1.86 (dddd, 1, $J$ = 14.2, 12.2, 3.9, 2.9), 1.64 (s, 3), 1.30 (t, 3, $J$ = 7.1); $^{13}$C NMR 179.4, 167.7, 144.2, 136.2, 83.9, 61.8, 42.7, 42.6, 30.7, 28.4, 24.3, 14.6; IR (neat) 1776, 1710. Anal. Calcd for $C_{14}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.45; H, 6.90.

The data for **44a**: $^1$H NMR 5.89 (ddd, 1, $J$ = 11.3, 7.4, 4.0), 5.74 (ddd, 1, $J$ = 11.3, 1.8, 0.7), 4.22 (q, 2, $J$ = 7.1), 2.79 (ddd, 1, $J$ = 12.3, 1.7, 1.0), 2.57 (dddd, 1, $J$ = 13.8, 4.4, 4.4, 1.6), 2.46−2.33 (m, 2), 2.35 (d, 1, $J$ = 12.3), 2.06 (ddt, 1, $J$ = 13.8, 11.3, 4.8), 1.63 (s, 3), 1.29 (t, 3, $J$ = 7.1); $^{13}$C NMR (partial) 135.4, 132.8, 82.8, 62.1, 56.9, 47.0, 33.6, 27.8, 24.5, 14.0; IR (neat) 1769, 1737. Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.28; H, 6.91.

**Oxidative Cyclization of Ethyl 1-(2-Methyl-2-butenyl)-2-oxocyclohexanecarboxylate (30b).** Reaction of $\beta$-keto ester **30b** (112 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (335 mg, 1.25 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 5 mL of degassed AcOH at 80 °C for 16 h followed by normal workup gave 108 mg of a pale yellow crude oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 2 mg (2%) of recovered **30b**, followed by 48 mg (40%) of a 2.25:1 mixture of **34b** and **35b**, 18 mg (15%) of a 7:3:1 mixture of **33b**, **34b**, and **35b**, 21 mg (17%) of **33b**, and 3 mg (2%) of ethyl 6-acetoxy-1-(2-methyl-2-butenyl)-2-oxocyclohexanecarboxylate. The calculated yields are 27% of **33b**, 32% of **34b**, and 13% of **35b**.

The data for **33b**: $^1$H NMR 5.38 (d, 1, $J$ = 0.9), 4.24 (q, 2, $J$ = 7.1), 2.78−2.61 (m, 2), 2.37−2.27 (m, 2), 1.96−1.78 (m, 4), 1.81 (s, 3), 1.66-1.61 (m, 1), 1.29 (t, 3, $J$ = 7.1); IR (neat) 1748, 1706. The data are identical to those previously reported.[19]

Partial $^1$H NMR data for **34b** were obtained from the mixture: $^1$H NMR 5.30 (br dq, 1, $J$ = 6.1, 1.5), 4.23 (q, 2, $J$ = 7.1), 3.33 (br d, 1, $J$ = 18.3), 2.44 (d, 1, $J$ = 18.3), 1.78 (d, 3, $J$ = 1.3), 1.30 (t, 3, $J$ = 7.1). The data are identical to those previously reported.[19]

Partial $^1$H NMR data for **35b** were obtained from the mixture: 4.90 (t, 2, $J$ = 1.9), 4.22 (q, 2, $J$ = 7.1), 1.29 (t, 3, $J$ = 7.1).

**Oxidative Cyclization of Ethyl 3-Methyl-2-oxo-1-(2-propenyl)cyclopentanecarboxylate (45).** Reaction of **45** (105 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (402 mg, 1.5 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 5 mL of degassed AcOH at 80 °C for 20 h followed by normal workup gave 104 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 32 mg (31%) of **46**, followed by 20 mg (19%) of a 1:1 mixture of **46** and **47**, 3 mg (3%) of acetates **48**, and 25 mg (24%) of a 2:3 mixture of lactones **50** and **49**. The calculated yields are 41% of **46**, 9% of **47**, 3% of **48**, 9% of **50**, and 15% of **49**.

The data for **46**: $^1$H NMR 5.58 (ddd, 1, $J$ = 9.1, 3.8, 2.2), 5.52 (br d, 1, $J$ = 9.1), 4.23 (q, 2, $J$ = 7.2), 3.23 (br d, 1, $J$ = 17.4), 2.68 (dd, 1, $J$ = 17.4, 3.8), 2.62−2.56 (m, 1), 2.22 (ddd, 1, $J$ = 13.6, 10.1, 1.9), 2.06 (ddd, 1, $J$ = 13.2, 10.1, 7.8), 1.87−1.77 (m, 1), 1.29 (t, 3, $J$ = 7.2), 1.11 (s, 3); $^{13}$C NMR 211.8, 171.5, 137.4, 124.6, 61.2, 56.4, 48.0, 44.4, 36.5, 29.9, 16.6, 14.2; IR (neat) 1760, 1727.

The data for **47** were obtained from the mixture: $^1$H NMR 6.09 (ddd, 1, $J$ = 9.3, 2.1, 1.1), 5.63 (ddd, 1, $J$ = 9.3, 3.7, 2.6), 4.26 (q, 2, $J$ = 7.1), 3.22 (br d, 1, $J$ = 17.5), 2.67 (dd, 1, $J$ = 17.5, 3.7), 2.66−2.59 (m, 1), 2.28 (ddd, 1, $J$ = 12.7, 10.1, 3.1), 2.04 (ddd, 1, $J$ = 13.1, 10.2, 7.3), 1.94−1.85 (m, 1), 1.30 (t, 3, $J$ = 7.1), 1.12 (s, 3); $^{13}$C NMR 212.2, 170.4, 132.1, 124.7, 61.3, 58.9, 49.9, 46.2, 33.1, 32.3, 19.5, 14.2.

The data for acetates **48**: $^1$H NMR 5.65−5.53 (m, 1), 5.17−5.03 (m, 2), 4.16 (q, 0.5 × 2, $J$ = 7.1), 4.12 (q, 0.5 × 2, $J$ = 7.1), 3.09−2.91 (m, 1), 2.79−2.69 (m, 1), 2.59−2.28 (m, 3), 2.05 (s, 0.5 × 3), 2.04 (s, 0.5 × 3), 1.91−1.81 (m, 1), 1.56 (s, 0.5 × 3), 1.41 (s, 0.5 × 3), 1.25 (t, 3, $J$ = 7.1).

Partial $^1$H NMR data for **49** were obtained from the mixture: 5.82−5.73 (m, 2), 4.25 (q, 2, $J$ = 7.1), 1.49 (s, 3), 1.31 (t, 3, $J$ = 7.2); IR (neat) of the mixture 1773, 1738.

Partial $^1$H NMR data for **50** were obtained from the mixture: 5.73 (br d, 1, $J$ = 6.6), 4.95 (dd, 1, $J$ = 8.2, 6.6), 4.24 (q, 2, $J$ = 7.1), 1.79 (dd, 3, $J$ = 1.4, 1.1), 1.30 (t, 3, $J$ = 7.1).

**Oxidative Cyclization of 2-Dodecyl-2-(2-propenyl)-cyclopentanone (51).** Reaction of **51** (73 mg, 0.25 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (201 mg, 0.75 mmol), and $Cu(OAc)_2 \cdot H_2O$ (50 mg, 0.25 mmol) in 2.5 mL of degassed AcOH at 80 °C for 12 h followed by normal workup gave 76 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 23 mg (32%) of a 7:1 mixture of **52** and **53**, followed by 14 mg (19%) of a 5:1 mixture of **52** and **53**, 7 mg (10%) of acetates **54**, and 5 mg (7%) of α-hydroxy ketones **55**. The calculated yields are 44% of **52**, 7% of **53**, 10% of **54**, and 7% of **55**.

The data for **52**: $^1$H NMR 5.84 (dddd, 1, $J$ = 9.0, 6.7, 2.3, 1.0), 5.55 (ddd, 1, $J$ = 9.0, 3.6, 2.7), 2.56−2.51 (m, 2), 2.05−1.88 (m, 4), 1.43−1.18 (m, 23), 0.88 (t, 3, $J$ = 6.6); $^{13}$C NMR 219.3, 132.8, 126.0, 48.9, 46.5, 33.2, 31.9, 31.6, 30.7, 30.4, 29.7, 29.6 (2C), 29.5, 29.3, 28.7, 24.2, 24.1, 22.7, 14.1; IR (neat) 1741. Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80. Found: C, 82.88; H, 11.32.

Partial $^1$H NMR data for **53** were obtained from the mixture: 5.66 (dd, 1, $J$ = 8.8, 1.7).

The data for acetates **54**: $^1$H NMR 6.0−5.9 (m, 1), 5.8−5.5 (m, 1), 5.1−5.0 (m, 2), 1.6−2.5 (m, 6), 2.14 (0.4 × 3, s), 2.135 (0.6 × 3, s), 1.0−1.4 (m, 22), 0.88 (t, 3, $J$ = 6.6).

The data for alcohols **55**: $^1$H NMR 5.8−5.5 (m, 1), 5.1−5.0 (m, 2), 4.9−4.8 (m, 1), 1.6−2.5 (m, 6), 1.0−1.4 (m, 22), 0.88 (t, 3, $J$ = 6.6).

**Oxidative Cyclization of 2-(2-Propenyl)cyclohexanone (56a).** Reaction of **56a** (138 mg, 1.0 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (1.073 g, 4.0 mmol), KOAc (496 mg, 5.0 mmol), and $Cu(OAc)_2 \cdot H_2O$ (200 mg, 1.0 mmol) in 10 mL of degassed AcOH at 80 °C for 24 h followed by normal workup gave 146 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 9 mg (6%) of recovered **56a**, followed by 43 mg (32%) of **57a**, 30 mg (22%) of a 20:1:1 mixture of **57a**, **58a**, and **61a**, 10 mg (7%) of a 1:1 mixture of acetates **59a** and **60a**, and 5 mg (4%) of acetate **62a**. The calculated yields are 51% of **57a**, 1% of **58a**, 3% of **59a**, 3% of **60a**, 1% of **61a**, and 3% of **62a**.

The data for **57a**: $^1$H NMR 5.94 (dt, 1, $J$ = 9.5, 3.4), 5.58 (dddd, 1, $J$ = 9.5, 5.9, 2.4, 1.5), 2.85−2.82 (m, 1), 2.75 (br dd, 1, $J$ = 18.6, 7.3), 2.61−2.56 (m, 1), 2.46 (br dd, 1, $J$ = 18.6, 3.4), 2.04−1.84 (m, 5), 1.57−1.51 (m, 1); $^{13}$C NMR 216.6, 129.9, 127.2, 47.7, 45.5, 36.9 (2C), 33.2, 16.9; IR (neat) 1729. The data are identical to those previously reported.[14]

Partial $^1$H NMR data for enone **58a** were obtained from the mixture: 6.94 (dt, 1, $J$ = 3.5, 10.1), 5.89−5.66 (m, 2), 5.11−4.96 (m, 2).

Partial $^1$H NMR data for enone **61a**[20] were obtained from the mixture: 6.73 (t, 1, $J$ = 4.2), 5.89−5.66 (m, 1), 5.11−4.96 (m, 2).

The data for **62a**: $^1$H NMR 5.84 (dt, 1, $J$ = 9.5, 3.6), 5.57 (dddd, 1, $J$ = 9.5, 5.9, 2.4, 1.7), 3.16 (br d, 1, $J$ = 18.1), 3.13 (m, 1), 2.92 (ddd, 1, $J$ = 18.1, 3.6, 1.7), 2.18−2.00 (m, 3), 2.11 (s, 3), 1.84−1.89 (m, 2), 1.73−1.65 (m, 1); $^{13}$C NMR 206.5, 169.2, 127.9, 125.9, 83.9, 49.2, 42.1, 42.0, 33.2, 21.7, 17.9; IR (neat) 1753, 1731.

**Oxidative Cyclization of 2-(2-Propenyl)cycloheptanone (56b).** $Mn(OAc)_3 \cdot 2H_2O$ (1120 mg, 4.18 mmol), $Cu(OAc)_2$ (126 mg, 0.696 mmol), and **56b** (106 mg, 0.696 mmol) were stirred in 8 mL of glacial acetic acid at 80 °C for 60 h. Normal workup and flash chromatography of the residue on silica gel (24:1 hexane/EtOAc) gave 10 mg (9%) of unreacted **56b**, followed by 33 mg (32%) of **57b** and 16 mg (11%) of **60b**.

The data for **57b**: $^1$H NMR 5.83 (m, 1), 5.63 (ddd, 1, $J$ = 9.8, 3.1, 3.0), 2.95 (m, 1), 2.74 (dddd, 1, $J$ = 10.2, 5.5, 5.1, 1.3), 2.56 (dddd, 1, $J$ = 17.5, 5.1, 5.1, 3.0), 2.25 (ddd, 1, $J$ = 17.5, 5.5, 1.8), 2.12 (m, 1), 1.81−1.65 (m, 3), 1.52 (m, 2), 1.24 (dddd, 1, $J$ = 13.5, 13.5, 5.9, 1.5), 1.02 (m, 1); $^{13}$C NMR 209.0, 129.5, 126.3, 49.9, 46.6, 34.5, 31.0, 30.4, 27.1, 25.9; IR (neat) 1716.

The data for **60b**: $^1$H NMR 5.73 (dddd, 1, $J$ = 18.0, 9.4, 7.6, 6.9), 5.12 (br d, 1, $J$ = 18.0), 5.09 (br d, 1, $J$ = 9.4), 2.91 (dd, 1, $J$ = 14.8, 6.9), 2.73 (ddd, 1, $J$ = 15.1, 6.4, 6.4), 2.59 (dd, 1, $J$ = 14.8, 7.6), 2.44 (ddd, 1, $J$ = 15.1, 6.7, 6.7), 2.24 (ddd, 1, $J$ = 14.6, 6.6, 3.0), 2.09 (s, 3), 1.77−1.35 (m, 7); $^{13}$C NMR 207.2, 170.1, 132.3, 119.0, 87.8, 40.4, 38.9, 34.6, 28.2, 23.8, 23.1, 20.1; IR (neat) 1738, 1708.

**Oxidative Cyclization of 2-(2-Propenyl)cyclooctanone (56c).** $Mn(OAc)_3 \cdot 2H_2O$ (582 mg, 2.17 mmol), $Cu(OAc)_2$ (66 mg, 0.36 mmol), and **56c** (60 mg, 0.36 mmol) were stirred in 8 mL of glacial acetic acid at 80 °C for 42 h. Normal workup and flash chromatography of the residue on silica gel (15:1 hexane/EtOAc) gave 18 mg (30%) of unreacted **56c**, followed by 20 mg (25%) of **63c**: $^1$H NMR 6.46 (d, 1, $J$ = 5.4), 5.37 (dt, 1, $J$ = 5.4, 4.7), 2.76 (m, 2), 2.23 (ddd, 1, $J$ = 14.6, 7.0, 4.2), 2.14−

1.91 (m, 2), 1.99 (s, 3), 1.79 (m, 2), 1.67−1.38 (m, 6); decoupled at 6.46, 5.34 (t, 1, $J = 4.7$), 2.23 (dd, 1, $J = 14.5, 6.8$); decoupled at 5.37, 6.51 (br s, 1); $^{13}$C NMR 194.7, 170.6, 147.7, 132.1, 66.8, 44.5, 36.6, 31.8, 31.4, 31.2, 27.0, 24.9, 21.0; IR (neat) 1734, 1699; UV (EtOH) $\lambda_{max}$ 229.8 nm ($\epsilon$ 5029). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.26; H, 8.41.

**Oxidative Cyclization of 1-Methyl-1-(2-propenyl)-2-tetralone (64).** Reaction of **64** (100 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (335 mg, 1.25 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 5 mL of degassed AcOH at 80 °C for 16 h followed by normal workup gave 92 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 59 mg (59%) of **65**, followed by 16 mg (16%) of a 2:1 mixture of **65** and **66**.

The data for **65**: $^1$H NMR 7.33−7.10 (m, 4), 5.70 (dddd, 1, $J = 9.3, 4.7, 2.0, 1.0$), 5.59 (br dt, 1, $J = 9.3, 3.3$), 3.39 (dd, 1, $J = 16.7, 5.2$), 3.19−3.17 (m, 1), 3.15 (dd, 1, $J = 16.7, 1.9$), 2.62 (d, 2, $J = 3.3$), 1.49 (s, 3); $^{13}$C NMR 213.6, 144.6, 132.9, 129.8, 128.4, 127.0, 126.7, 126.5, 125.8, 49.0, 48.3, 46.8, 39.0, 19.9; IR (neat) 1728.

The data for **66** were obtained from the mixture: $^1$H NMR 7.33−7.12 (m, 4), 5.72−5.65 (m, 1), 5.55 (ddd, 1, $J = 9.1, 2.5, 0.8$), 3.56 (dd, 1, $J = 17.4, 8.4$), 3.21 (dd, 1, $J = 17.4, 2.4$), 3.00 (dddd, 1, $J = 8.4, 5.5, 2.4, 1.4$), 2.84 (ddddd, 1, $J = 17.8, 5.5, 2.5, 2.4, 0.7$), 2.55 (ddd, 1, $J = 17.8, 4.4, 1.4$), 1.51 (s, 3); $^{13}$C NMR (partial) 137.2, 134.8, 128.4, 128.3, 126.7, 126.5, 124.8, 124.2, 42.2, 40.0, 39.2, 17.9.

**Oxidative Cyclization of 1,1-Bis(2-propenyl)-4a-methyl-3,4,4a,5,6,7-hexahydronaphthalen-2(1*H*)-one (67).** $Mn(OAc)_3 \cdot 2H_2O$ (363 mg, 1.35 mmol), $Cu(OAc)_2$ (109 mg, 0.60 mmol), and **67** (147 mg, 0.60 mmol) were stirred in 5 mL of glacial acetic acid at 80 °C for 10 h. Normal workup and flash chromatography of the residue on silica gel (30:1 hexane/EtOAc) gave 3 mg of **70**, followed by 12 mg of a 1:20 mixture of **70** and **68**, followed by 96.5 mg of **68** and 20 mg of a 1:1.2 mixture of **68** and **69**. The calculated yields of **68**, **69**, and **70** are 80%, 7.5%, and 2.5%, respectively.

The data for **68**: $^1$H NMR 5.90 (dddd, 1, $J = 17.9, 10.3, 7.5, 7.5$), 5.72 (dd, 1, $J = 4.1, 4.1$), 5.64 (ddd, 1, $J = 8.9, 5.4, 2.9$), 5.47 (br dd, 1, $J = 8.9, 4.9$), 5.02 (br d, 1, $J = 10.3$), 5.01 (br d, 1, $J = 17.9$), 2.92 (dd, 1, $J = 9.5, 5.4$), 2.70 (dd, 1, $J = 17.3, 4.9$), 2.50 (dd, 1, $J = 13.9, 7.5$), 2.35 (br d, 1, $J = 17.3$), 2.26 (dd, 1, $J = 13.9, 7.5$), 2.03 (m, 3), 1.76 (d, 1, $J = 12.8$), 1.62−1.40 (m, 4), 0.94 (s, 3); $^{13}$C NMR 218.5, 146.5, 135.0, 132.8, 124.9, 122.8, 117.4, 52.9, 46.1, 46.0, 45.5, 41.0, 40.4, 33.0, 29.2, 25.4, 19.2; IR (neat) 1727, 1650.

Partial data for **69**: $^1$H NMR ($CDCl_3$) 5.45 (dd, 1, $J = 4.7, 2.9$), 5.40 (m, 2), 0.90 (s, 3); $^1$H NMR ($C_6D_6$) 6.12 (dddd, 1, $J = 17.1, 10.1, 6.9, 6.9$), 5.29 (dd, 1, $J = 9.2, 2.8$), 5.23 (dd, 1, $J = 4.6, 2.7$), 5.14 (m, 1), 0.88 (s, 3).

The data for **70**: $^1$H NMR 5.87 (dddd, 1, $J = 17.0, 10.2, 7.3, 7.3$), 5.56 (dd, 1, $J = 4.7, 3.2$), 5.04 (m, 2), 5.02 (br d, 1, $J = 10.2$), 4.96 (br d, 1, $J = 17.0$), 2.85 (d, 1, $J = 8.0$), 2.51−2.33 (m, 3), 2.32 (dd, 1, $J = 12.9, 8.0$), 2.02 (m, 2), 1.78 (d, 1, $J = 12.9$), 1.65−1.48 (m, 4), 1.30 (m, 1), 0.97 (s, 3); $^{13}$C NMR 218.4, 150.8, 147.3, 135.3, 122.4, 117.1, 109.3, 55.2, 52.0, 49.6, 45.1, 40.4, 36.7, 32.3, 29.2, 24.9, 18.4; IR (neat) 1758, 1642.

**Oxidative Cyclization of Ethyl 2-Methyl-2-(2-propenyl)acetoacetate (71a).** Reaction of **71a** (92 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (804 mg, 3 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 10 mL of degassed AcOH at 80 °C for 48 h followed by normal workup gave 101 mg of a pale yellow oil. Purification by flash chromatography (4:1 hexane/EtOAc) afforded 40 mg (30%) of acetate **75a**, followed by 9 mg (7%) of a 20:1 mixture of acetates **74a** and **75a** and 31 mg (23%) of **74a**. The calculated yields are 30% of **74a** and 30% of **75a**.

The data for **74a**: $^1$H NMR 6.77 (br ddd, 1, $J = 10.3, 2.1, 0.8$), 6.10 (dd, 1, $J = 10.3, 2.2$), 5.73 (dddd, 1, $J = 10.0, 5.4, 2.2, 2.1$), 4.18 (q, 2, $J = 7.1$), 2.77 (ddd, 1, $J = 13.0, 5.4, 2.0$), 2.11 (s, 3), 2.04 (dd, 1, $J = 13.0, 10.0$), 1.43 (s, 3), 1.24 (t, 3, $J = 7.1$); $^{13}$C NMR 195.0, 171.4, 170.0, 147.5, 129.8, 66.9, 61.9, 53.2, 39.5, 21.4, 21.0, 14.0; IR (neat) 1745, 1695. A sample of a 1:1 mixture of acetates **74a** and **75a** was submitted for CH analysis. Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.05; H 6.48.

The data for **75a**: $^1$H NMR 6.80 (ddd, 1, $J = 10.3, 3.1, 1.1$), 6.11 (dd, 1, $J = 10.3, 1.6$), 5.57 (dddd, 1, $J = 7.8, 5.1, 3.1, 1.6$), 4.19 (q, 2, $J = 7.1$), 2.69 (dd, 1, $J = 13.6, 7.8$), 2.23 (ddd, 1, $J = 13.6, 5.1, 1.1$), 2.10 (s, 3), 1.45 (s, 3), 1.26 (t, 3, $J = 7.1$); $^{13}$C NMR 196.2, 172.0, 170.1, 145.2, 129.8, 65.7, 61.5, 52.6, 37.9, 20.9, 19.9, 14.0; IR (neat) 1742, 1687.

**Oxidative Cyclization of Ethyl 2-(2(*E*)-Butenyl)-2-methylacetoacetate (71b).** Reaction of **71b** (99 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (804 mg, 3 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 10 mL of degassed AcOH at 80 °C for 48 h followed by normal workup gave 103 mg of a pale yellow oil. Purification by flash chromatography (4:1 hexane/EtOAc) gave 2 mg of recovered $\beta$-keto ester **71b** (2%), followed by 12 mg (10%) of acetate **75b**, 27 mg (20%) of a 1:2 mixture of acetates **75b** and **74b**, and 20 mg (17%) of acetate **74b**. The calculated yields are 30% of **74b** and 17% of **75b**.

The data for **74b**: $^1$H NMR 5.99 (br s, 1), 5.52 (br dd, 1, $J = 6.9, 4.8$), 4.16 (q, 2, $J = 6.9$), 2.69 (dd, 1, $J = 13.8, 6.9$), 2.15 (dd, 1, $J = 13.8, 4.8$), 2.11 (s, 3), 1.95 (s, 3), 1.42 (s, 3), 1.25 (t, 3, $J = 6.9$); $^{13}$C NMR 196.0, 172.4, 170.2, 156.1, 127.8, 68.2, 61.4, 51.9, 38.0, 20.8, 20.4, 20.3, 14.0; IR (neat) 1742, 1682. A sample of the mixture of acetates was submitted for CH analysis. Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.14. Found: C, 61.64; H, 7.30.

The data for **75b**: $^1$H NMR 5.98 (br s, 1), 5.81 (br dd, 1, $J = 9.6, 5.4$), 4.18 (q, 2, $J = 7.1$), 2.73 (dd, 1, $J = 13.2, 5.4$), 2.13 (s, 3), 1.92 (dd, 1, $J = 13.2, 9.6$), 1.91 (s, 3), 1.41 (s, 3), 1.25 (t, 3, $J = 7.1$); $^{13}$C NMR 194.7, 171.5, 170.0, 158.5, 127.6, 68.8, 61.7, 53.1, 39.4, 21.3, 20.8, 19.7, 14.0; IR (neat) 1743, 1684.

**Oxidative Cyclization of 3-Acetyl-4,5-dihydro-3-(2-propenyl)-2(3*H*)-furanone (76a).** Reaction of **76a** (93 mg, 0.55 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (951 mg, 3.55 mmol), and $Cu(OAc)_2$ (107 mg, 0.59 mmol) in 10 mL of glacial acetic acid at 80 °C for 40 h followed by normal workup gave 96 mg of crude product, which was purified by flash chromatography on silica gel (1:2:0.4 hexane/EtOAc/$CH_2Cl_2$) to yield 30 mg (24%) of **77a**, followed by 48 mg (39%) of **78a**.

The data for **77a**: $^1$H NMR 6.99 (ddd, 1, $J = 10.3, 3.0, 1.3$), 6.14 (dd, 1, $J = 10.3, 1.8$), 6.06 (dddd, 1, $J = 8.2, 5.4, 3.0, 1.8$), 4.46 (dt, 1, $J = 8.8, 7.2$), 4.39 (dt, 1, $J = 8.8, 3.7$), 2.90 (ddd, 1, $J = 13.1, 7.2, 3.7$), 2.72 (ddd, 1, $J = 13.6, 5.4, 1.3$), 2.15 (dd, 1, $J = 13.6, 8.2$), 2.14 (m, 1), 2.11 (s, 3); $^{13}$C NMR 193.3, 174.1, 169.8, 148.6, 128.8, 66.7, 65.7, 53.8, 36.4, 33.4, 20.9; IR (neat) 1764, 1738, 1684.

The data for **78a**: $^1$H NMR 6.91 (ddd, 1, $J = 10.4, 2.1, 2.0$), 6.06 (dd, 1, $J = 10.4, 2.2$), 5.65 (dddd, 1, $J = 10.9, 5.3, 2.2, 2.1$), 4.43 (m, 1), 4.33 (m, 1), 2.70 (dd, 1, $J = 12.9, 10.9$), 2.48−2.42 (m, 2), 2.29 (ddd, 1, $J = 12.9, 5.3, 2.0$), 2.15 (s, 3); $^{13}$C NMR 193.5, 174.8, 170.2, 149.6, 127.9, 66.2, 65.2, 54.1, 36.4, 32.9, 20.9; IR (neat) 1777, 1744, 1679. Anal. Calcd for $C_{11}H_{12}O_5$: C, 58.78; H, 5.39. Found: C, 58.99; H, 5.58.

**Oxidative Cyclization of 3-Acetyl-3-(2-butenyl)-4,5-dihydro-2(3*H*)-furanone (76b).** $Mn(OAc)_3 \cdot 2H_2O$ (585 mg, 2.18 mmol), $Cu(OAc)_2$ (66 mg, 0.36 mmol), and **76b** (66 mg, 0.36 mmol) were stirred in 10 mL of glacial acetic acid at 80 °C for 24 h. Normal workup and flash chromatography of the residue on silica gel (1:2:0.4 hexane/EtOAc/$CH_2Cl_2$) provided 12 mg of unreacted **76b**, followed by 2 mg (2%) of **79b**, 15 mg (17%) of **77b**, and 23 mg (27%) of **78b**.

The data for **77b**: $^1$H NMR 6.01 (m, 2), 4.44 (dt, 1, $J = 8.8, 7.1$), 4.37 (dt, 1, $J = 8.8, 3.4$), 2.84 (ddd, 1, $J = 13.0, 7.1, 3.4$), 2.70 (dd, 1, $J = 13.8, 5.4$), 2.20−2.05 (m, 2), 2.13 (s, 3), 2.01 (d, 3, $J = 0.8$); $^{13}$C NMR 193.0, 174.6, 169.9, 159.8, 126.7, 68.0, 66.7, 53.4, 36.2, 33.5, 20.9, 20.7; IR (neat) 1765, 1743, 1666.

The data for **78b**: $^1$H NMR 5.93 (dq, 1, $J = 1.5, 1.5$), 5.67 (ddd, 1, $J = 10.8, 5.2, 1.9$), 4.42 (m, 1), 4.33 (m, 1), 2.66 (dd, 1, $J = 12.9, 10.8$), 2.42 (m, 1), 2.23 (dd, 1, $J = 12.9, 5.1$), 2.16 (s, 3), 1.99 (d, 3, $J = 0.9$); $^{13}$C NMR 193.2, 175.1, 170.3, 161.0, 125.7, 68.2, 65.3, 54.2, 36.4, 33.1, 20.8, 19.8; IR (neat) 1776, 1744, 1666. Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.36; H, 5.61.

**Partial data for 79b**: $^1$H NMR 5.82 (dd, 1, $J = 9.7, 2.0$), 5.54 (d, 1, $J = 10.1$), 5.50 (dd, 1, $J = 9.7, 2.8$), 4.39 (dd, 1, $J = 8.7, 5.4$), 4.30 (m, 1), 3.03 (ddd, 1, $J = 13.0, 5.5, 5.5$), 2.18 (s, 3), 2.20−2.00 (m, 2), 1.30 (d, 3, $J = 7.0$).

**Oxidative Cyclization of 1-Phenyl-6(*Z*)-nonen-1-one (80).** $Mn(OAc)_3 \cdot 2H_2O$ (439 mg, 1.64 mmol), $Cu(OAc)_2$ (49 mg, 0.27 mmol), and **80** (59 mg, 0.27 mmol) were stirred in 6 mL of glacial acetic acid at 80 °C for 60 h. Normal workup and flash chromatography of the residue on silica gel (20:1 hexane/EtOAc) gave 6 mg (10%) of recovered phenyl ketone **80**, followed by 9 mg (12%) of **83b**, 10 mg (13%) of **83a**, and 6 mg (8%) of **88**.

The data for **83b**: $^1$H NMR 7.97 (dd, 1, $J$ = 7.7, 1.5), 7.52 (ddd, 1, $J$ = 7.6, 7.6, 1.5), 7.36−7.28 (m, 2), 2.85 (ddd, 1, $J$ = 8, 8, 4), 2.66 (ddd, 1, $J$ = 8, 8, 8), 2.22−1.92 (m, 2), 2.13 (s, 3), 1.78−1.58 (m, 6), 0.86 (t, 3, $J$ = 7.3); $^{13}$C NMR 194.8, 169.7, 144.7, 133.5, 128.6, 128.5, 128.0, 126.8, 89.8, 47.3, 44.3, 37.7, 33.5, 28.5, 22.7, 21.4, 10.8; IR (neat) 1743, 1694.

The data for **83a**: $^1$H NMR 7.83 (dd, 1, $J$ = 7.8, 1.4), 7.49 (ddd, 1, $J$ = 7.6, 7.6, 1.4), 7.35−7.26 (m, 2), 3.32 (ddd, 1, $J$ = 10, 4, 4), 2.53 (ddd, 1, $J$ = 10, 10, 5), 2.22−2.06 (m, 2), 2.12 (s, 3), 1.92−1.75 (m, 6), 0.67 (t, 3, $J$ = 7.5); $^{13}$C NMR 196.1, 169.7, 144.9, 134.2, 132.7, 128.2, 126.5, 126.4, 90.2, 50.5, 39.9, 29.3, 28.1, 23.9, 21.2, 20.8, 8.3; IR (neat) 1744, 1705.

The data for **88**: $^1$H NMR 8.16 (dd, 1, $J$ = 8.3, 1.6), 7.57−7.40 (m, 3), 2.87−2.80 (m, 2), 2.71−2.48 (m, 2), 2.12−1.95 (m, 4), 2.01 (s, 3), 0.40 (t, 3, $J$ = 7.5); $^{13}$C NMR 204.1, 168.8, 143.6, 139.4, 134.6, 132.4, 127.9, 126.3, 123.7, 123.5, 75.0, 54.8, 33.7, 32.8, 30.1, 21.9, 6.9; IR (neat) 1742, 1658.

**Oxidation of (3aα,9*β*,9a*β*)-9-Ethyl-1,2,3,3a,9,9a-hexahydro-4*H*-benz[*f*]inden-4-one (81a)[22] and (3aα,9α,9aα)-9-Ethyl-1,2,3,3a,9,9a-hexahydro-4*H*-benz[*f*]inden-4-one (81b).**[22] Reaction of an inseparable 20:1 mixture of **81a** and **81b** (1 mg, 0.285 mmol) and $Mn(OAc)_3 \cdot 2H_2O$ (172 mg, 0.64 mmol) in 5 mL of glacial acetic acid at 80 °C for 48 h followed by normal workup and flash chromatography (10:1 hexane/EtOAc) provided 20 mg (31%) of a 3:2 mixture of **86** and **87**, followed by 7 mg (9%) of **83b**, 9 mg (12%) of **83a**, and 10 mg (13%) of **88**.

The data for **86**: $^1$H NMR 7.80 (dd, 1, $J$ = 7.8, 1.2), 7.51 (ddd, 1, $J$ = 7.6, 7.6, 1.5), 7.38−7.25 (m, 2), 3.69 (s, 1, OH), 2.66 (ddd, 1, $J$ = 8.4, 6.0, 2.4), 2.51 (ddd, 1, $J$ = 9.5, 9.5, 2.4), 2.25−1.23 (m, 8), 0.77 (t, 3, $J$ = 7.3); $^{13}$C NMR 203.6, 146.5, 139.4, 133.3, 129.5, 127.3, 127.1, 83.4, 49.8, 44.9, 42.9, 34.8, 32.2, 24.2, 11.5.

The data for **87**: $^1$H NMR (partial data) 7.30−7.20 (m, 3), 7.15 (dd, 1, $J$ = 6.9, 1.7), 4.00 (s, 1, OH), 3.13 (dd, 1, $J$ = 8.7, 3.7), 2.95 (m, 1), 0.89 (t, 3, $J$ = 7.3); $^{13}$C NMR 200.1, 140.8, 127.6, 127.5, 126.9, 126.8, 125.4, 77.8, 51.6, 49.9, 45.8, 36.2, 32.5, 20.0, 11.5.

IR of the mixture: ($CCl_4$) 3521, 1724, 1687.

**Hydrolysis of 83b To Give 86 and 87.** To 5 mL of 1 N NaOH solution was added a solution of **83b** (20 mg, 0.073 mmol) in 5 mL of ethanol. The resulting mixture was stirred at rt for 3 h. The mixture was neutralized by addition of 5 mL of 1 N HCl solution and extracted with $CH_2Cl_2$ (3 × 5 mL). The combined organic layers were washed with brine, dried ($Na_2SO_4$), and concentrated in vacuo to yield 14 mg (83%) of a 1:1 mixture of **86** and **87**.

**Oxidative Cyclization of 2-Methyl-2-(2-propenyl)-1,3-cyclopentanedione (89a).** Reaction of **89a** (76 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (303 mg, 1.125 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 2.5 mL of degassed AcOH at 80 °C for 2 h followed by normal workup gave 79 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 3 mg (4%) of a 2:1 mixture of **90a** and **92a**, followed by 52 mg (70%) of **90a**, 5 mg (6%) of a 1:1.5 mixture of **90a** and **91a**, and 4 mg (5%) of **91a**. The calculated yields are 75% of **90a**, 9% of **91a**, and 2% of **92a**.

The data for **90a**: $^1$H NMR 6.05 (dddd, 1, $J$ = 9.2, 6.6, 2.4, 1.1), 5.62 (ddd, 1, $J$ = 9.2, 3.0, 3.0), 3.15 (t, 1, $J$ = 6.6), 2.97 (d, 1, $J$ = 17.8), 2.80−2.61 (m, 3), 1.15 (s, 3); $^{13}$C NMR 213.8, 211.7, 133.4, 126.4, 57.4, 50.2, 47.7, 45.4, 12.6; IR (neat) 1769, 1732. The data are identical to those previously reported.[26]

The data for **91a**: $^1$H NMR 5.81 (dt, 1, $J$ = 8.8, 2.7), 5.27 (dd, 1, $J$ = 8.8, 2.9), 3.08 (br d, 1, $J$ = 17.5), 2.85−2.68 (m, 4), 1.24 (s, 3).

The $^1$H NMR data for **92a** were obtained from the mixture: 7.23 (s, 2), 5.57−5.42 (m, 1), 5.08 (br d, 1, $J$ = 10.7), 5.06 (br d, 1, $J$ = 16.6), 2.28 (d, 2, $J$ = 7.4), 1.15 (s, 3).

**Oxidative Cyclization of 2-(2(*E*)-Butenyl)-2-methyl-1,3-cyclopentanedione (89b).** $Mn(OAc)_3 \cdot 2H_2O$ (436 mg, 1.62 mmol), $Cu(OAc)_2$ (118 mg, 0.65 mmol), and **89b** (108 mg, 0.65 mmol) were stirred in 8 mL of glacial acetic acid at 85 °C for 2 h. Normal workup and flash chromatography of the residue on silica gel (8:1 hexane/EtOAc and 2:1 hexane/EtOAc) gave 6 mg (6%) of **92b** as a 3:2 mixture of *E*/*Z* isomers, followed by 27 mg (25%) of **90b**, 22 mg (20%) of a 1:2 mixture of **90b** and **91b**, and 10 mg (9%) of **91b**. The calculated yields of **90b** and **91b** are 32% and 23%, respectively.

The data for **90b**: $^1$H NMR 5.27 (br s, 1), 2.93 (d, 1, $J$ = 18.2), 2.93 (d, 1, $J$ = 6.6), 2.74 (dd, 1, $J$ = 18.2, 6.6), 2.63 (ddq, 1, $J$ = 16.9, 3.8, 1.9), 2.54 (ddq, 1, $J$ = 16.9, 2.4, 2.4), 1.82 (br s, 3), 1.13 (s, 3); $^{13}$C NMR 213.9, 211.7, 142.2, 119.0, 56.6, 50.2, 49.2, 45.9, 22.1, 12.4; IR (neat) 1777, 1732.

The data for **91b**: $^1$H NMR 5.61 (br d, 1, $J$ = 9.7), 5.24 (dd, 1, $J$ = 9.7, 2.8), 3.20 (m, 1), 3.10 (d, 1, $J$ = 19.2), 2.82 (dd, 1, $J$ = 8.1, 4.0), 2.54 (dd, 1, $J$ = 19.2, 8.1), 1.22 (s, 3), 1.20 (d, 3, $J$ = 8.2); $^{13}$C NMR 210.9, 203.8, 133.6, 130.1, 59.9, 50.2, 43.0, 38.5, 16.4, 9.8; IR (neat) 1770, 1728.

The data for **92b**: $^1$H NMR (*E*-isomer) 7.23 (s, 2), 5.48 (m, 1), 5.07 (m, 1), 2.43 (br d, 2, $J$ = 7.8), 1.55 (br s, 3), 1.17 (s, 3); partial data for *Z*-isomer 7.22 (s, 2), 2.32 (br d, 2, $J$ = 7.5), 1.56 (br s, 3), 1.13 (s, 3).

**Oxidative Cyclization of 2-Methyl-2-(2-propenyl)-1,3-cyclohexanedione (93).** $Mn(OAc)_3 \cdot 2H_2O$ (677 mg, 2.53 mmol), $Cu(OAc)_2$ (115 mg, 0.63 mmol), and **93** (105 mg, 0.63 mmol) were stirred in 12 mL of glacial acetic acid at 80 °C for 5 h. Normal workup and flash chromatography of the residue on silica gel (10:1 hexane/EtOAc) gave 18 mg (17%) of **96**: $^1$H NMR 7.06 (dd, 1, $J$ = 9.8, 6.5), 6.46 (d, 1, $J$ = 9.8), 3.36 (ddd, 1, $J$ = 6.5, 3.6, 3.3), 2.05−1.92 (m, 3), 1.79−1.57 (m, 3), 1.23 (s, 3); $^{13}$C NMR 209.7, 203.4, 146.6, 132.7, 63.2, 49.1, 41.9, 29.9, 17.4, 15.5; IR (neat) 1731, 1674.

**Oxidative Cyclization of Ethyl 1-(3-Butenyl)-2-oxocyclopentanecarboxylate (97a).** Reaction of **97a** (105 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (335 mg, 1.25 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 10 mL of degassed AcOH at 80 °C for 2.5 h followed by normal workup gave 101 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 4 mg (4%) of recovered **97a**, followed by 22 mg (22%) of a 1:4.5 mixture of **99a** and **98a**, 25 mg (25%) of a 1:3.5:8 mixture of **99a**, **98a**, and **100a**, 10 mg (10%) of **100a**, and (elution with 10:1 hexane/EtOAc) 12 mg (12%) of **101a**. The calculated yields are 25% of **98a**, 10% of **99a**, 25% of **100a**, and 12% of **101**.

The data for **98a** were obtained from the mixture: $^1$H NMR 5.67−5.65 (m, 2), 4.20 (q, 2, $J$ = 7.1), 2.74−2.71 (m, 1), 2.57−2.15 (m, 6), 1.97 (ddd, 1, $J$ = 13.2, 9.7, 6.6), 1.69 (dddd, 1, $J$ = 12.7, 9.9, 4.8, 2.2), 1.27 (t, 3, $J$ = 7.1); $^{13}$C NMR (partial) 172.2, 126.5, 125.7, 61.3, 59.1, 45.9, 34.6, 32.6, 31.4, 25.4, 14.1.

The data for **99a** were determined from the mixture: $^1$H NMR 5.90 (dddd, 1, $J$ = 11.0, 8.1, 2.0, 0.8), 5.81 (ddd, 1, $J$ = 11.0, 6.4, 4.6), 4.20 (q, 2, $J$ = 7.1), 2.98 (br dt, 1, $J$ = 2.0, 8.1), 2.62 (dddd, 1, $J$ = 13.2, 10.7, 4.0, 0.8), 2.53−2.21 (m, 4), 2.10 (ddd, 1, $J$ = 13.3, 9.3, 5.9), 1.98−1.87 (m, 2), 1.27 (t, 3, $J$ = 7.1); $^{13}$C NMR (partial) 62.5, 49.3, 41.9, 35.5, 34.3, 21.2, 14.0; IR (neat) 1732, 1716.

The data for **100a**: $^1$H NMR 4.75 (t, 1, $J$ = 1.5), 4.71 (br s, 1), 4.22 (q, 2, $J$ = 7.1), 3.12 (d, 1, $J$ = 6.6), 2.67−2.55 (m, 2), 2.36 (ddd, 1, $J$ = 14.4, 5.8, 1.3), 2.25−2.19 (m, 4), 1.88−1.80 (m, 1), 1.28 (t, 3, $J$ = 7.1); $^{13}$C NMR 210.1, 171.2, 148.9, 109.8, 61.2, 57.2, 55.9, 35.6, 26.9, 26.7, 22.7, 14.1; IR (neat) 1742, 1712.

The data for **101a**: $^1$H NMR 4.95−5.05 (br s, 2), 5.01 (dd, 1, $J$ = 6, 6), 4.25 (q, 2, $J$ = 7.1), 2.70 (dddd, 1, $J$ = 13.9, 10.1, 2.7, 1.3), 2.53−2.38 (m, 3), 2.33 (ddd, 1, $J$ = 13.9, 11.9, 6.0), 2.06 (ddd, 1, $J$ = 13.8, 10.8, 6.2), 2.07−1.97 (m, 1), 1.91 (dddd, 1, $J$ = 13.8, 10.8, 2.8, 1.3), 1.30 (t, 3, $J$ = 7.1); $^{13}$C NMR (partial) 171.6, 170.9, 144.6, 115.1, 80.7, 61.9, 31.9, 29.0, 25.5, 24.7, 14.0; IR (neat) 1732.

**Oxidation of *β*-Keto Ester 100a to Lactone 101a.** A solution of **100a** (26 mg, 0.125 mmol) and $Mn(OAc)_3 \cdot 2H_2O$ (67 mg, 0.25 mmol) in 2.5 mL of degassed AcOH was stirred at 80 °C for 14 h until the solution turned bright blue, which

indicated that all of the Mn(III) was consumed. Normal workup afforded 23 mg of a 1:1 crude mixture of **100a** and **101a**.

**Oxidative Cyclization of Ethyl 1-(3-Butenyl)-2-oxocyclohexanecarboxylate (97b).** Reaction of $\beta$-keto ester **97b** (112 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (402 mg, 1.5 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 5 mL of degassed AcOH at 80 °C for 18 h followed by normal workup gave 105 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 10 mg (9%) of a 2:3 mixture of recovered **97b** and **98b**, followed by 22 mg (20%) of **100b**, 28 mg (25%) of a 1:1 mixture of **100b** and **99b**, 33 mg (30%) of a 3:1 mixture of **99b** and **100b**, and 3 mg (3%) of a 6:1 mixture of **99b** and **100b**. The calculated yields are 6% of **98b**, 37% of **99b**, and 40% of **100b**.

The $^1$H NMR data for **98b** were obtained from the mixture: 5.92 (dddd, 1, $J$ = 11.0, 7.8, 4.7, 1.4), 5.42 (ddd, 1, $J$ = 11.0, 5.5, 2.4), 4.23 (q, 2, $J$ = 7.2), 3.29−3.25 (m, 1), 2.48−2.26 (m, 3), 2.24−2.08 (m, 2), 2.04−1.82 (m, 3), 1.76 (ddd, 1, $J$ = 14.0, 2.9, 0.8), 1.68−1.58 (m, 1), 1.29 (t, 3, $J$ = 7.2).

The $^1$H NMR data for **99b** were obtained from the mixture: 5.88−5.83 (m, 2), 4.22 (q, 2, $J$ = 7.1), 2.81−2.77 (m, 1), 2.60 (br d, 2, $J$ = 4.8), 2.51−2.38 (m, 2), 2.36−2.19 (m, 2), 2.13−1.86 (m, 3), 1.62−1.55 (m, 1), 1.28 (t, 3, $J$ = 7.1). The data are identical to those previously reported.[26]

The data for **100b**: $^1$H NMR 4.92 (s, 1), 4.81 (s, 1), 4.22 (q, 2, $J$ = 7.1), 3.17 (br s, 1), 2.79−2.69 (m, 1), 2.60 (dddd, 1, $J$ = 13.6, 8.4, 6.5, 1.5), 2.51−2.45 (m, 1), 2.34 (ddt, 1, $J$ = 14.9, 1.0, 7.2), 2.81−1.98 (m, 5), 1.67−1.61 (m, 1), 1.29 (t, 3, $J$ = 7.1); $^{13}$C NMR 211.9, 172.5, 148.7, 111.2, 61.2, 57.8, 55.5, 37.6, 36.8, 32.7, 30.6, 18.9, 14.1; IR (neat) 1734, 1708.

**Oxidative Cyclization of Ethyl 2-Oxo-1-(4-pentenyl)-cyclopentanecarboxylate (97c)**. Reaction of **97c** (112 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (335 mg, 1.25 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 5 mL of degassed AcOH at 80 °C for 2.5 h followed by normal workup gave 104 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 4 mg (4%) of a 1:1 mixture of **100c** and **99c**, followed by 5 mg (5%) of **99c**, 4 mg (4%) of a 3:1 mixture of **99c** and **98c**, and 81 mg of polymeric material. The calculated yields are 1% of **98c**, 10% of **99c**, and 2% of **100c**.

Partial $^1$H NMR data for **98c** were obtained from the mixture: 5.91−5.84 (m, 2), 4.22 (q, 2, $J$ = 7.2), 2.84−2.75 (m, 1), 2.60 (m, 1), 1.25 (t, 3, $J$ = 7.2).

The data for **99c**: $^1$H NMR 5.83 (ddd, 1, $J$ = 10.5, 7.4, 7.0), 5.76 (ddd, 1, $J$ = 10.5, 7.4, 7.0), 4.14 (q, 2, $J$ = 7.1), 2.68 (dddd, 1, $J$ = 7.3, 7.3, 7.1, 0.9), 2.39−2.28 (m, 4), 2.27−2.01 (m, 3), 1.83 (ddt, 1, $J$ = 12.9, 1.1, 4.0), 1.55−1.46 (ddd, 1, $J$ = 14.6, 11.5, 4.4), 1.31−1.22 (m, 1), 1.22 (t, 3, $J$ = 7.1); $^{13}$C NMR 194.5, 173.1, 132.4, 129.1, 61.3, 61.1, 51.3, 32.8, 27.8, 27.7, 26.4, 23.6, 14.0; IR (neat) 1747, 1728.

Partial $^1$H NMR data for **100c** were obtained from the mixture: 4.88 (br s, 1), 4.81 (d, 1, $J$ = 1.0), 4.23 (q, 2, $J$ = 7.1), 3.28−3.20 (m, 1), 3.08−3.01 (m, 1), 1.23 (t, 3, $J$ = 7.1).

**Oxidative Cyclization of Methyl 1-(3(*Z*)-Hexenyl)-2-oxocyclopentanecarboxylate (102a).** Reaction of **102a** (116 mg, 0.52 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (416 mg, 1.55 mmol), and $Cu(OAc)_2$ (94 mg, 0.52 mmol) in 10 mL of AcOH at 80 °C for 25 h followed by normal workup provided 122 mg of crude product, which was purified by flash chromatography on silica gel (30:1 hexane/EtOAc) to yield 83 mg (72%) of a 5:2 mixture of **103a** and **104a**. **103a**: $^1$H NMR 5.47 (ddq, 1, $J$ = 15.4, 6.2, 1.2), 5.32 (ddq, 1, $J$ = 15.4, 7.5, 1.2), 3.75 (s, 3), 2.70 (br ddd, 1, $J$ = 10.6, 7.5, 6.3), 2.55 (ddd, 1, $J$ = 12.5, 12.2, 4.2), 2.34 (br d, 1, $J$ = 5.7), 2.20 (ddd, 1, $J$ = 12.6, 7.0, 1.2), 2.08−1.79 (m, 4), 1.74−1.58 (m, 2), 1.66 (dd, 3, $J$ = 6.2, 1.2); decoupling at $\delta$ 5.32 collapsed the peak at $\delta$ 2.69 (br dd, 1, $J$ = 10.6, 6.3); $^{13}$C NMR 214.4, 171.9, 131.4, 125.7, 57.3, 52.2, 50.8, 48.2, 36.4, 27.2, 23.5, 17.9, 17.5. **104a**: $^1$H NMR (partial data) 3.76 (s, 3), 3.05 (dddd, 1, $J$ = 10, 8, 6, 2.3); decoupling at $\delta$ 5.32 collapsed the peak at $\delta$ 3.04 (ddd, 1, $J$ = 10, 6, 2.3); $^{13}$C NMR 214.1, 171.9, 130.4, 125.1, 57.3, 52.2, 50.8, 43.3, 36.8, 27.3, 24.4, 17.5, 13.1; IR (neat) 1756, 1729.

**Oxidative Cyclization of Ethyl 1-(3(*Z*)-Hexenyl)-2-oxocyclohexanecarboxylate (102b).** $Mn(OAc)_3 \cdot 2H_2O$ (284 mg, 1.06 mmol), $Cu(OAc)_2$ (77 mg, 0.42 mmol), and **102b** (107 mg, 0.42 mmol) were stirred in 10 mL of glacial acetic acid at 85 °C for 15 h. Normal workup and flash chromatography of the residue on silica gel (30:1 hexane/EtOAc) recovered 12 mg (11%) of unreacted **102b**, followed by 70 mg (75%) of a 5:2 mixture of **103b** and **104b**. **103b**: $^1$H NMR 5.48 (br dd, 1, $J$ = 13.5, 5.8), 5.39 (m, 1), 4.21 (q, 2, $J$ = 7.1), 2.70−2.36 (m, 4), 2.18−1.84 (m, 6), 1.63 (d, 3, $J$ = 5.8), 1.62 (m, 1), 1.40 (m, 1), 1.28 (t, 3, $J$ = 7.1); $^{13}$C NMR 214.6, 172.7, 131.8, 126.0, 61.1, 57.9, 51.2, 46.4, 35.8, 35.2, 27.7, 26.6, 20.7, 18.1, 14.1. **104b**: $^1$H NMR (partial data) 4.22 (q, 2, $J$ = 7.1), 1.70 (d, 3, $J$ = 5.8), 1.29 (t, 3, $J$ = 7.1); $^{13}$C NMR 214.6, 173.0, 130.7, 125.5, 61.1, 57.7, 50.8, 41.3, 36.0, 35.4, 27.9, 26.6, 20.8, 14.1, 13.1; IR (neat) 1734, 1715.

**Oxidative Cyclization of Methyl 1-(3(*Z*)-Hexenyl)-3-methyl-2-oxocyclopentanecarboxylate (102c).** $Mn(OAc)_3 \cdot 2H_2O$ (107 mg, 0.40 mmol), $Cu(OAc)_2$ (29 mg, 0.16 mmol), and **102c** (38 mg, 0.16 mmol) were stirred in 3.5 mL of glacial acetic acid at 70 °C for 12 h. Normal workup and flash chromatography of the residue on silica gel (30:1 hexane/EtOAc) provided 27 mg (72%) of an 8:1 mixture of **103c** and **104c**. **103c**: $^1$H NMR 5.47 (dq, 1, $J$ = 15.1, 6.4), 5.30 (ddq, 1, $J$ = 15.1, 8.3, 1.4), 3.75 (s, 3), 2.50 (dddd, 1, $J$ = 12.8, 12.8, 4.2, 1.5), 2.24 (m, 1), 2.17 (br dd, 1, $J$ = 12.6, 7.3), 2.10−2.00 (m, 2), 1.90 (ddd, 1, $J$ = 12.8, 10.9, 4.7), 1.67 (dd, 3, $J$ = 6.4, 1.4), 1.72−1.49 (m, 3), 0.92 (s, 3); decoupling at $\delta$ 5.30 collapsed the peak at $\delta$ 2.24 (br dd, 1, $J$ = 10.0, 6.8), indicating that the H is axial and the propenyl substituent is equatorial; $^{13}$C NMR 216.0, 172.2, 129.2, 127.7, 58.2 (q), 54.2, 52.3, 50.7 (q), 36.4, 26.4, 25.7, 25.6, 18.0, 17.8. **104c**: $^1$H NMR (partial data) 3.76 (s, 3), 2.68 (m, 1), 0.88 (s, 3); $^{13}$C NMR (partial data) 128.7, 126.1, 48.1, 36.7, 17.3, 13.3; IR (neat) 1750, 1729.

**Oxidative Cyclization of Ethyl 2-(3-Butenyl)-2-methyl-3-oxobutanoate (105a).** $Mn(OAc)_3 \cdot 2H_2O$ (516 mg, 1.92 mmol), $Cu(OAc)_2$ (108 mg, 0.59 mmol), and **105a** (117 mg, 0.59 mmol) were stirred in 5 mL of glacial acetic acid at 80 °C for 40 h. Normal workup and flash chromatography of the residue on silica gel (30:1 hexane/EtOAc) gave 20 mg (17%) of unreacted **105a**, followed by 1 mg (1%) of **107a**, 13 mg (10%) of **110a**, and 48 mg (32%) of **109a**.

The data for **107a**: $^1$H NMR 5.75 (m, 2), 4.19 (q, 2, $J$ = 7.1), 2.92 (m, 1), 2.63 (ddd, 1, $J$ = 13.3, 8.0, 5.3), 2.45 (m, 1), 2.23 (m, 2), 1.96 (m, 1), 1.38 (s, 3), 1.25 (t, 3, $J$ = 7.1).

The data for **109a**: $^1$H NMR 6.05 (s, 1), 4.66 (s, 2), 4.17 (q, 2, $J$ = 7.1), 2.53 (m, 1), 2.39 (m, 1), 2.26 (ddd, 1, $J$ = 19.0, 5.0, 4.7), 2.13 (s, 3), 1.91 (ddd, 1, $J$ = 13.5, 8.6, 5.0), 1.39 (s, 3), 1.23 (t, 3, $J$ = 7.1); $^{13}$C NMR 196.3, 172.4, 170.1, 157.0, 123.7, 64.7, 61.4, 52.9, 32.9, 24.0, 20.6, 20.3, 14.0; IR (neat) 1740, 1732, 1682.

The data for **110a**: $^1$H NMR 9.77 (s, 1), 6.62 (br s, 1), 4.17 (q, 2, $J$ = 7.1), 2.62−2.38 (m, 3), 1.91 (ddd, 1, $J$ = 13.6, 8.6, 5.0), 1.43 (s, 3), 1.23 (t, 3, $J$ = 7.1); $^{13}$C NMR 204.0, 193.8, 171.9, 153.1, 138.5, 61.7, 54.0, 32.8, 20.1, 19.6, 14.0; IR (neat) 1728, 1694, 1680.

**Oxidative Cyclization of Ethyl 2-Methyl-3-oxo-2-(4-pentenyl)butanoate (105b).** $Mn(OAc)_3 \cdot 2H_2O$ (643 mg, 2.40 mmol), $Cu(OAc)_2$ (109 mg, 0.60 mmol), and **105b** (127 mg, 0.60 mmol) were stirred in 25 mL of glacial acetic acid at 80 °C for 40 h. Normal workup and flash chromatography of the residue on silica gel (20:1 hexane/EtOAc) gave 12 mg of **107b**, followed by 29 mg of a 2:3 mixture of **107b** and unreacted **105b**, 8 mg of **106b**, 9 mg of a 3:2 mixture of **106b** and **109b**, and 3 mg of **109b**. The calculated yields of **107b**, **106b**, and **109b** are 19%, 8%, and 4%, respectively.

The data for **106b**: $^1$H NMR 6.04 (dd, 1, $J$ = 13.2, 1.5), 5.97 (dd, 1, $J$ = 13.2, 2.9), 5.25 (m, 1), 4.15 (q, 2, $J$ = 7.1), 2.36 (m, 1), 2.03 (s, 3), 2.22−1.92 (m, 2), 1.70 (m, 2), 1.38 (s, 3), 1.25 (m, 1), 1.23 (t, 3, $J$ = 7.1); $^{13}$C NMR 190.1, 172.4, 170.1, 133.4, 129.0, 72.0, 61.6, 58.0, 32.1, 27.8, 21.1, 20.2, 17.8, 14.0; IR (neat) 1738, 1732, 1698.

The data for **107b**: $^1$H NMR 5.62 (m, 2), 4.25 (q, 2, $J$ = 7.1), 3.13 (m, 1), 2.58−2.40 (m, 2), 2.28−2.03 (m, 3), 1.37 (s, 3), 1.43−1.21 (m, 2), 1.30 (t, 3, $J$ = 7.1); $^{13}$C NMR 210.3, 174.2, 130.3, 129.6, 61.1, 57.7, 43.5, 35.2, 24.5, 23.2, 22.6, 14.1; IR (neat) 1734, 1700.

The data for **109b**: $^1$H NMR 6.08 (s, 1), 4.55 (s, 2), 4.14 (q, 2, $J$ = 7.1), 2.50−1.94 (m, 2), 2.12 (s, 3), 1.79−1.45 (m, 2), 1.40

(s, 3), 1.34−1.20 (m, 2), 1.21 (t, 3, $J$ = 7.1); $^{13}$C NMR 199.9, 173.6, 172.4, 149.3, 127.0, 66.6, 61.3, 58.2, 34.1, 31.1, 23.4, 23.1, 20.8, 14.0; IR (neat) 1738, 1735, 1685.

**Oxidative Cyclization of Ethyl 2-(3(*Z*)-Hexenyl)-2-methyl-3-oxobutanoate (111).** $Mn(OAc)_3 \cdot 2H_2O$ (422 mg, 1.57 mmol), $Cu(OAc)_2$ (72 mg, 0.39 mmol), and **111** (89 mg, 0.39 mmol) were stirred in 6 mL of glacial acetic acid at 80 °C for 40 h. Normal workup and flash chromatography of the residue on silica gel (30:1 hexane/EtOAc) gave 12 mg (14%) of **112** containing 5−10% of the *Z*-isomer, followed by 25 mg (28%) of unreacted **111** and 11 mg (10%) of **113** containing 5−10% of the *Z*-isomer.

The data for **112**: (*E*-isomer) $^1$H NMR 5.43 (dq, 1, $J$ = 15.3, 5.6), 5.34 (br dd, 1, $J$ = 15.3, 4.9), 4.18 (q, 2, $J$ = 7.1), 2.54−2.30 (m, 4), 1.76 (m, 1), 1.65 (d, 3, $J$ = 5.6), 1.62−1.41 (m, 2), 1.27 (s, 3), 1.26 (t, 3, $J$ = 7.1); $^{13}$C NMR 207.3, 172.9, 134.1, 124.3, 61.3, 56.2, 46.9, 42.7, 36.8, 29.5, 21.1, 17.8, 14.1; (*Z*-isomer) $^1$H NMR (partial data) 5.20 (ddq, 1, $J$ = 10.8, 9.1, 1.7); IR (neat) 1739, 1715.

The data for **113**: (*E*-isomer) $^1$H NMR 5.50 (dq, 1, $J$ = 15.3, 6.4), 5.29 (ddq, 1, $J$ = 15.3, 7.5, 1.6), 5.16 (d, 1, $J$ = 11.9), 4.29 (dq, 1, $J$ = 10.7, 7.1), 4.18 (dq, 1, $J$ = 10.7, 7.1), 2.49 (ddd, 1, $J$ = 13.9, 3.3, 3.3), 2.44 (m, 1), 2.15 (s, 3), 1.80 (m, 1), 1.65 (dd, 3, $J$ = 6.4, 1.6), 1.49−1.21 (m, 2), 1.32 (s, 3), 1.30 (t, 3, $J$ = 7.1); $^{13}$C NMR 200.9, 172.1, 170.0, 130.5, 127.3, 78.7, 61.9, 56.7, 47.5, 36.1, 27.6, 20.9, 20.6, 17.9, 13.9; (*Z*-isomer) $^1$H NMR (partial data) 2.12 (s, 3), 1.34 (s, 3); IR (neat) 1755, 1744, 1724.

**Oxidative Cyclization of Ethyl 2-Oxo-1-(phenylmethyl)cyclopentanecarboxylate (114).** Reaction of **114** (123 mg, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (335 mg, 1.25 mmol), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in 5 mL of degassed AcOH at 80 °C for 2 h followed by normal workup gave 136 mg of a pale yellow oil. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 36 mg (30%) of a 3:1 mixture of **115** and recovered **114**, followed by 12 mg (10%) of **115**, 6 mg (5%) of a 2:1 mixture of **115** and ethyl 2-oxo-1-(phenylmethyl)-cyclopent-3-enecarboxylate (enone), 9 mg (7%) of enone, 3 mg (2%) of a 1:1 mixture of enone and ethyl 3-acetoxy-2-oxo-1-(phenylmethyl)cyclopentanecarboxylate (acetates), and 45 mg (37%) of a 1:1 mixture of acetates. The calculated yields are 35% of **115**, 10% of enone, and 39% of acetates.

The data for **115**: $^1$H NMR 7.25−6.96 (m, 4), 4.27 (q, 2, $J$ = 7.1), 3.89 (br d, 1, $J$ = 16.8), 3.36 (d, 1, $J$ = 16.8), 3.28 (d, 1, $J$ = 5.6), 2.74 (br ddd, 1, $J$ = 12.1, 10.3, 2.2), 2.34−2.25 (m, 1), 2.17−2.01 (m, 2), 1.32 (t, 3, $J$ = 7.1); $^{13}$C NMR (partial) 130.2, 128.6, 128.3, 127.5, 127.4, 127.1, 61.0, 55.8, 51.2, 45.3, 29.7, 29.4, 14.2; IR (neat) 1738, 1709.

The data for enone: $^1$H NMR 7.58 (dt, 1, $J$ = 5.7, 2.7), 7.26−7.09 (m, 5), 6.07 (dt, 1, $J$ = 5.7, 2.2), 4.19 (q, 2, $J$ = 7.1), 3.27 (s, 2), 3.16 (br ddd, 1, $J$ = 19.3, 2.7, 2.2), 2.72 (br ddd, 1, $J$ = 19.3, 2.7, 2.2), 1.25 (t, 3, $J$ = 7.1).

The data for acetates: $^1$H NMR 7.28−7.06 (m, 4), 5.30 (dd, 0.5 × 1, $J$ = 10.7, 8.5), 4.64 (dd, 0.5 × 1, $J$ = 11.7, 8.3), 4.19 (q, 0.5 × 2, $J$ = 7.1), 4.18 (q, 0.5 × 2, $J$ = 7.1), 3.29−3.12 (m, 2), 2.41 (dd, 0.5 × 1, $J$ =5.9, 13.3), 2.37−2.16 (m, 2), 2.11 (s, 0.5 × 3), 2.10 (s, 0.5 × 3), 2.01−1.79 (m, 1.5), 1.29 (t, 0.5 × 3, $J$ = 7.1), 1.25 (t, 0.5 × 3, $J$ = 7.1).

**Oxidative Cyclization of Ethyl 3-Methyl-2-oxo-7-decenoate (118).** A solution of $\beta$-keto ester **118** (46 mg, 0.2 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (214 mg, 0.8 mmol), and $Cu(OAc)_2 \cdot H_2O$ (40 mg, 0.2 mmol) in 5 mL of degassed AcOH was stirred under $N_2$ for 56 h at 60 °C. Normal workup yielded 41 mg of a pale yellow oil. Purification by flash chromatography (10:1 hexane/EtOAc) gave 5 mg (10%) of recovered **118**, followed by 5 mg (10%) of **119**, 2 mg (4%) of a 2:1 mixture of **121** and **120**, and 20 mg (45%) of a 17:1:1.7:0.1 mixture of **123**, **124**, **122**, and **125**.

**Oxidative Cyclization of Ethyl 1-Methyl-2-oxo-6-(1(*E*)-propenyl)cyclohexanecarboxylate (119).** Reaction of pure **119** (44 mg, 0.2 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (134 mg, 0.5 mmol), and $Cu(OAc)_2 \cdot H_2O$ (40 mg, 0.2 mmol) in 5 mL of degassed AcOH at 80 °C for 16 h followed by normal workup gave 47 mg of a pale yellow oil. Purification by flash chromatography (10:1 hexane/EtOAc) afforded 36 mg (83%) of a 10:1 mixture of **123** and **122**.

The data for **123**: $^1$H NMR 5.80 (ddd, 1, $J$ = 17.3, 10.5, 5.9), 5.19 (d, 1, $J$ = 17.3), 5.16 (d, 1, $J$ = 10.5), 4.19 (q, 2, $J$ = 7.1), 2.88 (br d, 1, $J$ = 5.9), 2.77 (br d, 1, $J$ = 4.1), 2.63 (br d, 1, $J$ = 5.1), 2.06 (dddd, 1, $J$ = 13.6, 11.3, 5.1, 4.8), 1.76 (dddd, 1, $J$ = 13.4, 11.3, 5.2, 4.1), 1.70 (br ddd, 1, $J$ = 13.4, 8.1, 4.8), 1.48 (br ddd, 1, $J$ = 13.6, 8.1, 5.2), 1.33 (s, 3), 1.27 (t, 3, $J$ = 7.1); $^{13}$C NMR 213.2, 171.7, 133.9, 117.5, 61.5, 61.1, 53.3, 49.1, 48.7, 23.6, 19.5, 17.7, 14.1; IR (neat) 1752, 1728. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.98; H, 8.26.

Partial data for **122** were determined from the mixture. $^1$H NMR 6.95 (ddd, 1, $J$ = 10.2, 5.8, 1.7), 6.09 (br d, 1, $J$ = 10.2), 5.58−5.55 (m, 1), 1.73 (br d, 3, $J$ = 6.8), 1.35 (s, 3), 1.22 (t, 3, $J$ = 7.1).

**Oxidative Cyclization of 120 and 121.** Reaction of 30 mg (0.15 mmol) of a 1:2 mixture of **120** and **121**, respectively, $Mn(OAc)_3 \cdot 2H_2O$ (100 mg, 0.375 mmol), and $Cu(OAc)_2 \cdot H_2O$ (30 mg, 0.15 mmol) in 5 mL of degassed AcOH at 80 °C for 16 h followed by normal workup gave 26 mg of a pale yellow oil. Purification by flash chromatography (10:1 hexane/EtOAc) afforded 21 mg (70%) of a 1:2 mixture of **124** and **125**.

Partial data for **124** were determined from the mixture: $^1$H NMR 5.77 (ddd, 1, $J$ = 17.2, 10.3, 6.2), 5.20 (ddd, 1, $J$ = 17.2, 1.5, 1.5), 5.12 (ddd, 1, $J$ = 10.3, 1.5, 1.5), 4.21 (q, 2, $J$ = 7.1), 2.76 (br d, 1, $J$ = 6.2), 2.63 (br d, 1, $J$ = 4.9), 2.47 (br d, 1, $J$ = 3.7), 1.41 (s, 3), 1.27 (t, 3, $J$ = 7.1).

Partial data for **125** were determined from the mixture. $^1$H NMR 6.98−6.89 (m, 1), 6.11 (ddd, 1, $J$ = 10.2, 2.0, 1.6), 5.48 (br t, 1, $J$ = 6.9).

**Oxidative Cyclization of Methyl 1-(2(Z),6(*Z*)-Nondienyl)-2-oxocyclopentanecarboxylate (126).** $Mn(OAc)_3 \cdot 2H_2O$ (160 mg, 0.60 mmol), $Cu(OAc)_2$ (48 mg, 0.26 mmol), and **126** (70 mg, 0.26 mmol) were stirred in 7 mL of glacial acetic acid at 80 °C for 15 h. Normal workup and flash chromatography of the residue on silica gel (30:1 hexane/EtOAc) provided 8 mg of unreacted **126**, followed by 6 mg of a 3:2 mixture of **126** and **128**, followed by 21 mg of a 1.3:4.3:1 mixture of **126**, **128**, and **129**. The calculated yields of **128** and **129** are 23% and 5%, respectively.

The data for **128**: $^1$H NMR 5.54−5.31 (m, 2), 5.28 (m, 1), 3.76 (s, 3), 3.21 (dd, 1, $J$ = 17.0, 2.1), 2.66−2.49 (m, 4), 2.17−1.74 (m, 8), 0.96 (t, 3, $J$ = 7.4); IR (neat) 1760, 1732. The NMR spectral data are very similar to those of **8e**.

Partial data for **129**: $^1$H NMR 3.79 (s, 3), 0.95 (t, 3, $J$ = 7.5).

**Oxidative Cyclization of Methyl 1-(3(*Z*)-Hexenyl)-2-oxo-3-(2-propenyl)cyclopentanecarboxylate (131).** $Mn(OAc)_3 \cdot 2H_2O$ (100 mg, 0.37 mmol), $Cu(OAc)_2$ (30 mg, 0.17 mmol), and **131** (44 mg, 0.17 mmol) were stirred in 3.5 mL of glacial acetic acid at 70 °C for 12 h. Normal workup and flash chromatography of the residue on silica gel (40:1 hexane/EtOAc) provided 36 mg (82%) of a 9:1 mixture of **133** and **134**. **133**: $^1$H NMR 4.96 (m, 1), 4.83 (m, 1), 3.76 (s, 3), 2.85 (dddd, 1, $J$ = 16.4, 2.9, 2.7, 2.7), 2.52 (dddd, 1, $J$ = 12.8, 12.8, 4.5, 1.8), 2.33−2.22 (m, 2), 2.12−1.96 (m, 3), 1.92−1.81 (m, 3), 1.70−1.50 (m, 4), 0.89 (t, 3, $J$ = 7.5); $^{13}$C NMR 212.7, 172.1, 151.7, 106.8, 59.1, 57.8, 56.5, 52.3, 47.4, 38.6, 36.7, 26.2, 25.6, 23.9, 23.2, 10.4. **134**: $^1$H NMR (partial data) 5.00 (m, 1), 4.85 (m, 1), 3.74 (s, 3), 2.67 (m, 1), 0.84 (t, 3, $J$ = 7.5); $^{13}$C NMR (partial data) 151.0, 106.6, 55.8, 52.2, 44.9, 35.9, 35.2, 27.0, 24.9, 22.4, 19.0, 9.6; IR (neat) 1754, 1730.

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**Supporting Information Available:** Complete experimental details for preparation of the cyclization substrates; $^1$H and $^{13}$C NMR spectra of many compounds (123 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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