Pergamon

Tetrahedron 58 (2002) 3171–3175

TETRAHEDRON

Environmentally friendly TPDS-mediated free radical ring expansion of α-haloalkyl cyclic β-keto esters

Masaaki Sugi[a] and Hideo Togo[a,b,*]

[a]*Department of Chemistry, Graduate School of Science and Technology, Chiba University, Yayoi-cho 1-33, Inage-ku, Chiba 263-8522, Japan*

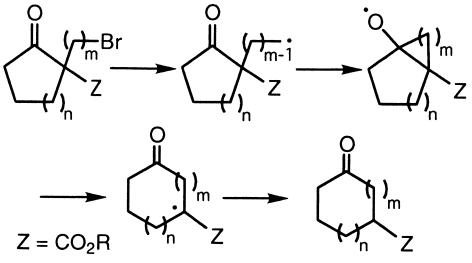
[b]*Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho 1-33, Inage-ku, Chiba 263-8522, Japan*

Received 4 February 2002; accepted 1 March 2002

Abstract—Reactivities of tetraphenyldisilane (TPDS), tris(trimethylsilyl)silane, and tributyltin hydride in the radical ring expansion of α-haloalkyl cyclic β-keto esters were examined. Among these reagents, TPDS was found most effective for the preparation of medium-sized cyclic compounds in terms of yields and ring-expansion/reduction selectivity.

1. Introduction

Recently, free radical reactions have become important in organic synthesis, since functional group conversion of organic compounds under mild reaction conditions is critical for the preparation of natural products and biologically active compounds.[1] Tributyltin hydride[2] and tris(trimethylsilyl)silane[3] are well-known reagents for these radical reactions, though the former reagent is highly toxic and the complete removal of the tin species from the reaction products is difficult, while the latter one is a less stable oil under aerobic conditions for storage. Radical cyclization reactions in *5-exo-trig* and *6-exo-trig* manner are a most powerful and versatile method for the construction of five- and six-membered cyclic systems.[4] However, the direct construction of a medium-sized ring skeleton by radical cyclization is normally not so useful because of poor yields of the cyclization products.[5] Thus, the construction of these compounds have been carried out by using non-radical methods extensively.[6] On the other hand, since their pioneering work on intramolecular alkyl radical addition to a carbonyl group with tributyltin hydride,[7] Beckwith[8] and Dowd[9] have reported a interesting free-radical ring expansion of α-halomethyl- and α-halopropyl cyclic β-keto esters to one-carbon and three-carbon ring-expanded cyclic keto esters, respectively, in *3-exo-trig* and *5-exo-trig* manner and subsequent β-cleavage in refluxing benzene solutions of tributyltin hydride in the presence of AIBN. Baldwin has also reported a radical ring expansion of α-(haloalkyl) β-stannylcyclohexanone with tributyltin hydride to form the corresponding ring expanded cycloalkenones.[10] These methods are efficient for the construction of medium-sized cyclic compounds and the reaction is very attractive and important, since these types of ring expansion are specific radical reactions and may be applicable to a wide range of functional groups of various ring size. However, highly toxic tin species are required for the preparation of these ring-expanded compounds. Therefore, use of radical reactions with organotin reagents cannot be considered in the chemical and pharmaceutical industries, even if results of the radical reactions for organic synthesis are excellent and effective. Very recently, treatment of α-halomethyl β-keto esters with SmI_2 in THF in the presence of an activator such as MeOH, HMPA, NiI_2 was reported to give the corresponding one-carbon ring-expanded products in good yields.[11] However, this reagent cannot be used for the three-carbon ring expansion reactions and one-carbon extension of acyclic α-halomethyl β-keto esters. As a part of our study on the synthetic application of 1,1,2,2-tetraphenyldisilane (TPDS) to organic synthesis as a radical reagent,[12] we report herein TPDS-mediated radical ring expansion of β-haloalkyl cyclic β-keto esters to form ring-expanded cyclic keto esters through the radical cyclization of the initially formed carbon radicals to the carbonyl group in *exo-trig* manner, followed by β-cleavage of the



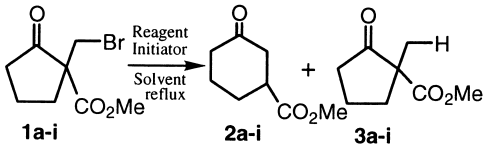
Scheme 1.

Keywords: 1,1,2,2-tetraphenyldisilane; medium-sized cyclic ketones; ring expansion.

* Corresponding author. Fax: +81-43-290-2874; e-mail: togo@scichem.schiba-u.ac.jp

0040–4020/02/$ - see front matter
PII: S0040-4020(02)00241-7

Table 1. Ring expansion of cyclic β-keto ester **1a-i** with various radical reagents

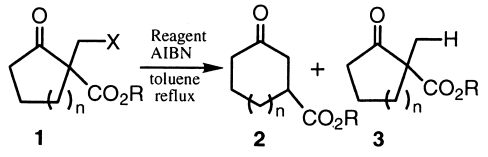


Entry	Reagent (equiv.)	Solvent	Yields (%)	
			2a-i	**3a-i**
1	H_3PO_2 (5.0)	EtOH[a]	ca. 20	ca. 30
2	$PhSiH_3$ (1.2)	Tolune[b]	3[c]	0
3	Ph_2SiH_2 (1.2)	Tolune[b]	47[d]	Trace
4	Bu_3SnH (1.2)	Tolune[a]	65	Trace
5	$(TMS)_3SiH$ (1.2)	Tolune[a]	64	Trace
6	$Ph_4Si_2H_2$ (1.2)	Tolune[a]	66	Trace
7	$Ph_4Si_2H_2$ (1.2)	Tolune[a,e]	61	Trace
8	$Ph_4Si_2H_2$ (1.2)	AcOEt[a]	59	Trace
9	$Ph_4Si_2H_2$ (1.2)	AcOEt[f]	3[g]	20

[a] Slow addition of AIBN with a dropping funnel.
[b] Slow addition of benzoyl peroxide with a dropping funnel.
[c] Compound **1a-i** was recovered in 81% yield.
[d] Compound **1a-i** was recovered in 36% yield.
[e] $Mg(ClO_4)_2$ was added.
[f] Et_3B was used as an initiator, and the reaction was carried out at rt.
[g] Compound **1a-i** was recovered in 64% yield.

resulting bicyclic alkoxy radical intermediate (Scheme 1). The reactivities were compared with those of other typical radical reagents such as tributyltin hydride, tris(trimethylsilyl)silane, etc. under the same conditions.

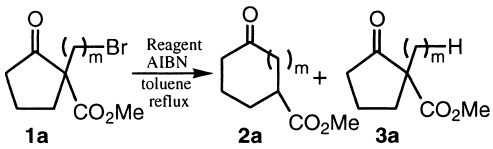
Table 2. Reactivities of TPDS, $(TMS)_3SiH$, and Bu_3SnH in ring expansion of cyclic β-keto esters **1**



Entry	*n*	R	X **1**	Reagent[a]	Yields (%)	
					2	**3**
1	1	Me	Br (**1a**)	$Ph_4Si_2H_2$	66	Trace
2				$(TMS)_3SiH$	64	Trace
3				Bu_3SnH	65	Trace
4		Me	I	$Ph_4Si_2H_2$	64	Trace
5				$(TMS)_3SiH$	65	Trace
6				Bu_3SnH	47	22
7	2	Et	Br (**1b**)	$Ph_4Si_2H_2$	67	Trace
8				$(TMS)_3SiH$	65	Trace
9				Bu_3SnH	20	68
10	3	Me	Br (**1c**)	$Ph_4Si_2H_2$	64	Trace
11				$(TMS)_3SiH$	52	18
12				Bu_3SnH	24	63
13	4	Me	Br (**1d**)	$Ph_4Si_2H_2$	48	Trace
14				$(TMS)_3SiH$	48	21
15				Bu_3SnH	39	45
16	8	Me	I (**1e**)	Ph_4SiH_2	53	9
17				$(TMS)_3SiH$	54	28
18				Bu_3SnH	15	57

[a] Substrate/radical reagent/AIBN=1/1.2/3–5.

Table 3. Reactivities of TPDS, $(TMS)_3SiH$, and Bu_3SnH in ring expansion of cyclic β-keto esters **1a**



Entry	*m*, **1a**	Reagent[a]	Yields (%)	
			2a	**3a**
1	1 (**i**)	$Ph_4Si_2H_2$	66	Trace
2		$(TMS)_3SiH$	64	Trace
3		Bu_3SnH	65	Trace
4	2 (**ii**)	$Ph_4Si_2H_2$	0	86
5	3 (**iii**)	$Ph_4Si_2H_2$	47	25
6		$(TMS)_3SiH$	25	42
7		Bu_3SnH	Trace	78
8	4 (**iv**)	$Ph_4Si_2H_2$	5	60

[a] Substrate/radical reagent/AIBN=1/1.2/3–5.

2. Results and discussion

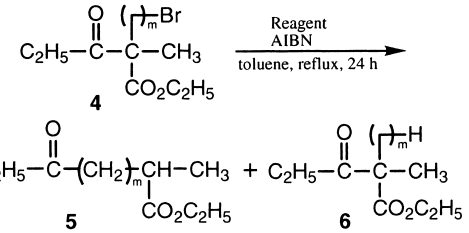
Ring expansion of methyl 1-bromomethyl-2-oxocyclopentanoate with various radical reagents, such as phosphinic acid, phenylsilane, diphenylsilane, tributyltin hydride, tris(trimethylsilyl)silane, and TPDS, in the presence of AIBN, Et_3B, or peroxide was carried out, and the results are shown in Table 1.

All reactions were carried out by the dropwise addition of a radical initiator to the refluxing solution of cyclic bromoalkyl β-keto esters in the presence of a radical reagent through a dropping funnel. The results suggest that phenylsilane did not work at all (entry 2), and phosphinic acid showed moderate reactivity, though the ratio of ring-expanded compound **2a-i** to the direct reduction product **3a-i** was poor (entry 1).

Surprisingly, diphenylsilane gave the ring-expanded product in moderate yield together with a trace amount of the direct reduction product (entry 3). However, much excess amount of peroxide is required. TPDS, tributyltin hydride, and tris(trimethylsilyl)silane showed almost the same reactivity to give the ring-expanded compound **2a-i** in good yields, together with trace amounts of the direct reduction product **3a-i** (entries 4–6) and starting material **1a-i** (~10%). So, here, there is no difference in the reactivity among TPDS, tributyltin hydride, and tris(trimethylsilyl)silane. Moreover, there is no effect of a Lewis acid such as $Mg(ClO_4)_2$ and $Yb(OTf)_3$ on the formation of ring-expanded ketones (**2a-i**, entry 7). The reaction initiated by Et_3B at room temperature markedly reduced the formation of the ring-expanded ketone **2a-i** and the starting bromide **1a-i** was mainly recovered (entry 9).

The effect of ring size in the TPDS-mediated ring expansion was examined and the reactivity was compared with those of tris(trimethylsilyl)silane and tributyltin hydride as shown in Table 2. Totally, TPDS gave the ring expansion products

Table 4. Reactivities of TPDS, $(TMS)_3SiH$, and Bu_3SnH in chain extension of acyclic β-keto esters **4**



4 **5** **6**

Entry	*m*, **4**	Reagent[a]	Yields (%)	
			5	**6**
1	1 (**i**)	$Ph_4Si_2H_2$	75	Trace
2		$(TMS)_3SiH$	76	Trace
3		Bu_3SnH	42	36
4	3 (**iii**)	$Ph_4Si_2H_2$	31	37
5		$(TMS)_3SiH$	34	43
6		Bu_3SnH	7	71

[a] Substrate/radical reagent/AIBN=1/1.2/3–5.

2 in better yields than those obtained with tributyltin hydride, though it showed almost the same reactivity as that of tris(trimethylsilyl)silane. The effect of the arm size in the bromoalkyl group was studied as shown in Table 3.

Again, the same reactivity of bromomethyl compound **1a-i** was observed in TPDS, tris(trimethylsilyl)silane, and tributyltin hydride (entries 1–3), and these three reagents did not give the two-carbon ring-expanded product at all with compound **1a-ii**; instead, the direct reduction product was formed (entry 4). Reaction of 3-bromopropyl β-keto ester **1a-iii** with TPDS gave a three-carbon ring-expanded product in moderate yield, though the same reactions with tris(trimethylsilyl)silane and tributyltin hydride were not so effective (entries 5–7). These results come from the fact that Si–H bond in tris(trimethylsilyl)silane is 5 kcal/mol stronger than Sn–H bond in tributyltin hydride, and probably Si–H bond in TPDS is slightly stronger than that in tris(trimethylsilyl)silane.[3]

Chain extension of acyclic bromoalkyl β-keto esters was carried out and the reactivity was compared with those of tris(trimethylsilyl)silane and tributyltin hydride as shown in Table 4. Here again, TPDS showed almost the same reactivity as those with tris(trimethylsilyl)silane, and tributyltin hydride showed poor results (entries 4–6).

3. Conclusion

TPDS and tris(trimethylsilyl)silane generally showed no remarkable difference in their good reactivities towards the radical ring expansion reaction, while the same reaction with tributyltin hydride gave poor yields of ring-enlarged products. In view of its stability (stable crystals in air), less toxicity, and easy handling, TPDS is a useful reagent for the preparation of medium-sized ring compounds through the radical ring expansion of α-haloalkyl cyclic β-keto esters.

4. Experimental

4.1. General

^1H NMR spectra were recorded on 400 and 500 MHz spectrometers, and ^{13}C NMR spectra were recorded on 100 and 125 MHz spectrometers. Chemical shifts are reported as ppm downfield from tetramethylsilane (TMS) in δ units. *J*-Values are given in Hz. 3-Nitrobenzyl alcohol was used as the matrix of mass spectra (FAB). Kieselgel 60 F254 was used for TLC, Silica Gel 60 (Kanto Kagaku) was used for column chromatography, and Wakogel B-5F was used for preparative TLC. Solvents were purified and dried by standard techniques.

4.2. General procedure using TPDS with Et_3B

Et_3B in THP (0.6 ml, 1 mol/l) was added into a mixture of α-haloalkyl β-keto ester (0.5 mmol) and TPDS (0.6 mmol) in a solvent (10 ml) under aerobic conditions.

After stirring for 4 h, the same amount of Et_3B was added again and the obtained mixture was stirred overnight at room temperature. After the reaction, the solvent was removed and the residue was purified by column chromatography using a mixture of hexane and ethyl acetate (5:1).

4.3. General procedure using TPDS with AIBN

AIBN (1.5–2.5 mmol) in toluene (10–15 ml) was added dropwise over 8 h using a dropping funnel to a refluxing solution of α-haloalkyl β-keto ester (0.5 mmol) and TPDS (0.6 mmol) in toluene (10 ml) and the obtained mixture was stirred overnight at the same temperature. After the reaction, the solvent was removed and the residue was purified by column chromatography using a mixture of hexane and ethyl acetate (5:1–10:1).

4.4. General procedure using tris(trimethylsilyl)silane and AIBN

AIBN (1.5 mmol) in toluene (10 ml) was added dropwise over 8 h using a dropping funnel to a refluxing solution of α-haloalkyl β-keto ester (0.5 mmol) and $(TMS)_3SiH$ (0.6 mmol) in toluene (10 ml) and the obtained mixture was stirred overnight at the same temperature. The mixture was purified as described in the general procedure using TPDS and AIBN.

4.5. General procedure using tributyltin hydride and AIBN

AIBN (1.5 mmol) in toluene (10 ml) was added dropwise over 8 h using a dropping funnel to a refluxing solution of α-haloalkyl β-keto ester (0.5 mmol) and Bu_3SnH (0.6 mmol) in toluene (10 ml) and the obtained mixture was stirred overnight at the same temperature. The mixture was purified as described in the general procedure using TPDS and AIBN.

4.5.1. Methyl 3-oxocyclohexanoate 2a-i. Oil; IR (neat) 2950, 2870, 1740, 1720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=3.71 (3H, s), 2.81 (1H, m), 2.56 (2H, d,

J=8.2 Hz), 2.44–2.28 (2H, m), 2.16–2.02 (2H, m), 1.90–1.69 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ=209.2 (q), 174.2 (q), 52.1 (p), 43.1 (s), 43.1 (t), 40.2 (s), 27.7 (s), 24.5 (s); MS (EI): m/z 156; HRMS (EI) Found: m/z 156.0789, Calcd for $C_8H_{12}O_3$: M=156.0786.

4.5.2. Ethyl 3-oxocycloheptanoate 2b. Oil; IR (neat) 2980, 2940, 2860, 1740, 1700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.15 (2H, q, J=7.2 Hz), 2.81 (1H, dd, J=11.0, 15.6 Hz), 2.73–2.66 (2H, m), 2.58–2.44 (2H, m), 2.10 (1H, m), 1.98–1.61 (5H, m), 1.26 (3H, t, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=212.2 (q), 174.5 (q), 60.8 (s), 45.5 (s), 43.5 (s), 41.2 (t), 33.2 (s), 28.3 (s), 27.9 (s), 14.1 (p); MS (FAB): m/z 185; HRMS (FAB) Found: m/z 185.1160, Calcd for $C_{10}H_{17}O_3$: M+H=185.1178.

4.5.3. Methyl 3-oxocyclooctanoate 2c. Oil; IR (neat) 2940, 2860, 1730, 1700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.70 (3H, s), 2.94 (1H, s), 2.94 (1H, m), 2.80 (1H, t, J=13.2 Hz), 2.42 (2H, m), 2.04–1.63 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ=214.5 (q), 174.8 (q), 51.9 (p), 42.9 (s), 42.8 (s), 42.7 (t), 29.7 (s), 27.2 (s), 24.8 (s) 23.2 (s); MS (EI): m/z 184; HRMS (EI) Found: m/z 184.1085, Calcd for $C_{10}H_{16}O_3$: M=184.1099.

4.5.4. Methyl 3-oxocyclononanoate 2d. Oil; IR (neat) 2930, 2870, 1740, 1700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.66 (3H, s), 3.02 (1H, m), 2.85 (1H, dd, J=11.3, 13.8 Hz), 2.63 (1H, dd, J=2.7, 13.8 Hz), 2.49 (2H, m), 1.96–1.32 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ=215.0 (q), 175.7 (q), 52.0 (p), 44.3 (s), 43.7 (s), 41.2 (t), 29.2 (s), 25.6 (s), 25.5 (s), 24.1 (s), 22.9 (s); MS (EI): m/z 198; HRMS (EI) Found: m/z 198.1064, Calcd for $C_{11}H_{18}O_3$: M=198.2629.

4.5.5. Methyl 3-oxocyclotridecanoate 2e. Oil; IR (neat) 2930, 2860, 1740, 1710 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.69 (3H, s), 2.98 (1H, m), 2.85 (1H, dd, J=8.9, 16.9 Hz), 2.74 (1H, dd, J=3.4, 16.9 Hz), 2.55 (1H, m), 2.35 (1H, m), 1.79–1.11 (18H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ=210.2 (q), 175.7 (q), 51.9 (p), 43.5 (s), 42.5 (s), 39.6 (t), 29.5 (s), 26.2 (s), 26.14 (s), 26.11 (s), 25.5 (s), 24.6 (s), 24.3 (s), 23.8 (s), 23.7 (s); MS (EI): m/z 254; HRMS (EI) Found: m/z 254.1863, Calcd for $C_{15}H_{26}O_3$: M=254.1882.

4.5.6. Methyl 5-oxocyclooctanoate 2a-iii. Oil; IR (neat) 2950, 2860, 1740, 1700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.64 (3H, s), 2.65–2.26 (4H, m), 2.18–1.92 (5H, m), 1.87–1.50 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ=210.9 (q), 176.7 (q), 51.6 (p), 41.9 (t), 41.8 (s), 29.9 (s), 24.4 (s); MS (FAB): m/z 185; HRMS (FAB) Found: m/z 185.1167, Calcd for $C_{10}H_{17}O_3$: M+1=185.1178.

4.5.7. Ethyl 2-methyl 4-oxohexanoate 5-i. Oil; IR (neat) 2980, 2940, 1730, 1720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.13 (2H, q, J=7.1 Hz), 2.55–2.37 (3H, m), 2.58–2.44 (2H, m), 1.25 (3H, t, J=7.1 Hz), 1.18 (3H, d, J=7.0 Hz), 1.06 (3H, t, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=209.5 (q), 175.9 (q), 60.6 (s), 45.3 (s), 36.1 (s), 34.8 (t), 17.2 (s), 14.2 (s), 7.7 (s); MS (EI): m/z 172; HRMS (EI) Found: m/z 172.1094, Calcd for $C_9H_{16}O_3$: M=172.1098.

4.5.8. Ethyl 2-methyl 6-oxooctanoate 5-iii. Oil; IR (neat) 2980, 2940, 1740, 1720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.13 (2H, q, J=7.0 Hz), 2.47–2.35 (5H, m), 1.70–1.30 (4H, m), 1.26 (3H, t, J=7.0 Hz), 1.15 (3H, d, J=7.0 Hz), 1.05 (3H, t, J=7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=211.3 (q), 176.6 (q), 60.2 (s), 42.1 (s), 39.4 (t), 35.8 (s), 33.2 (s), 21.5 (s), 17.0 (p), 14.2 (p), 7.8 (p); MS (EI): m/z 185; HRMS (EI) Found: m/z 200.1412, Calcd for $C_{11}H_{20}O_3$: M=200.1412.

Acknowledgements

We are grateful for the financial support from a Grant-in-Aid for Developmental Scientific Research (13554028) from the Ministry of Education, Science, Sport and Culture of Japan.

References

1. (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon: Oxford, 1986. (b) Motherwell, W. B.; Crich, D. *Free Radical Chain Reactions in Organic Synthesis*; Academic: New York, 1992. (c) Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; Wiley: Paris, 1995. (d) *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, 2001.
2. (a) Neumann, W. P. *Synthesis* **1987**, 665. (b) Curran, D. P. *Synthesis* **1988**, 417. (c) Curran, D. P. *Synthesis* **1988**, 489.
3. (a) Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188. (b) Chatgilialoglu, C.; Ferreri, C.; Gimisis, T. *The Chemistry of Organic Silicon Compounds*, Vol. 2; Wiley: New York, 1998; Chapter 25.
4. Giese, B.; Kopping, B.; Gobel, T.; Dickhaut, J.; Thoma, G.; Kulicke, K. J.; Trach, F. *Organic Reactions*; *Radical Cyclization Reactions*, Vol. 48; Wiley: New York, 1996; Chapter 2.
5. *endo-trig* Cyclization of iodoalkyl vinyl ketones and iodoalkyl acrylates with Bu_3SnH/AIBN gave the corresponding medium-sized cyclic ketones and lactones in moderate to low yields. (a) Porter, N. A.; Magnin, D. R.; Wright, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 2787. (b) Porter, N. A.; Chang, V. H. T. *J. Am. Chem. Soc.* **1987**, *109*, 4976. (c) Porter, N. A.; Chang, V. H. T.; Magnin, D. R.; Wright, B. T. *J. Am. Chem. Soc.* **1988**, *110*, 3554. (d) Porter, N. A.; Lacker, B.; Chang, V. H. T.; Magnin, D. R. *J. Am. Chem. Soc.* **1989**, *111*, 8309. (e) Cox, N. J. G.; Mills, S. D.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1313. 8-*endo-trig* Cyclization of 4-pentenyl α-bromoacetate with Bu_3SnH/AIBN proceeded to give lactones in moderate to low yields. (f) Lee, E.; Yoon, C. H.; Lee, T. H. *J. Am. Chem. Soc.* **1992**, *114*, 10981. (g) Lee, E.; Yoon, C. H.; Lee, T. H.; Kim, S. Y.; Ha, T. J.; Sung, Y. S.; Park, S. H.; Lee, S. *J. Am. Chem. Soc.* **1998**, *120*, 7469.
6. (a) Schaeffer, J. P.; Bloomfield, J. *J. Org. React.* **1967**, *15*, 1. (b) Gutsche, C. D.; Redmore, D. *Carbocyclic Ring Expansion Reactions*; Academic: New York, 1968. (c) Hesse, M. *Ring Enlargement in Organic Chemistry*; VCH: Weinheim, 1991.
7. Beckwith, A. L. J.; Kazlauskas, R.; Syner-Lyons, M. R. *J. Org. Chem.* **1983**, *48*, 4718.
8. (a) Beckwith, A. L. J.; O'Shea, D. M.; Gerba, S.; Westwood, S. W. *J. Chem. Soc., Chem. Commun.* **1987**, 666.

(b) Beckwith, A. L. J.; O'Shea, D. M.; Westwood, S. W. *J. Am. Chem. Soc.* **1988**, *110*, 2565.

9. (a) Dowd, P.; Choi, S. C. *J. Am. Chem. Soc.* **1987**, *109*, 6548. (b) Dowd, P.; Choi, S. C. *J. Am. Chem. Soc.* **1987**, *109*, 3493. (c) Dowd, P.; Choi, S. C. *Tetrahedron Lett.* **1989**, *30*, 6129. (d) Dowd, P.; Choi, S. C. *Tetrahedron* **1989**, *45*, 77. (e) Dowd, P.; Choi, S. C. *Tetrahedron Lett.* **1991**, *32*, 565. (f) Zhang, W.; Dowd, P. *Tetrahedron Lett.* **1992**, *33*, 3285. Reviews: (g) Dowd, P.; Zhang, W. *Chem. Rev.* **1993**, *93*, 2091. (h) Yet, L. *Tetrahedron* **1999**, *55*, 9349 and references cited therein.
10. (a) Baldwin, J. E.; Adlington, R. M.; Robertson, J. *J. Chem. Soc., Chem. Commun.* **1988**, 1404. (b) Baldwin, J. E.; Adlington, R. M.; Robertson, J. *Tetrahedron* **1989**, *45*, 909.
11. (a) Hasegawa, E.; Kitazume, T.; Suzuki, K.; Tosaka, E. *Tetrahedron Lett.* **1998**, *39*, 4059. (b) Chung, S. H.; Cho, M. S.; Choi, J. Y.; Kwon, D. W.; Kim, Y. H. *Synlett* **2001**, 1266.
12. (a) Yamazaki, O.; Togo, H.; Matsubayashi, S.; Yokoyama, M. *Tetrahedron Lett.* **1998**, *39*, 1921. (b) Yamazaki, O.; Togo, H.; Matsubayashi, S.; Yokoyama, M. *Tetrahedron* **1999**, *55*, 3735. (c) Yamazaki, O.; Togo, H.; Yokoyama, M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2891. (d) Yamazaki, O.; Togo, H.; Yamaguchi, K.; Yokoyama, M. *J. Org. Chem.* **2000**, *65*, 5440. (e) Togo, H.; Matsubayashi, S.; Yamazaki, O.; Yokoyama, M. *J. Org. Chem.* **2000**, *65*, 2816. (f) Ryokawa, A.; Togo, H. *Tetrahedron* **2001**, *57*, 5915.