

Triethylborane-Induced Radical Reaction of Alkynylgallium with α -Halo Carbonyl Compounds

Shin-ichi Usugi, Hideki Yorimitsu, Hiroshi Shinokubo, and Koichiro Oshima*

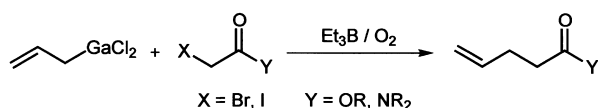
Department of Material Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606-8501

(Received July 8, 2002)

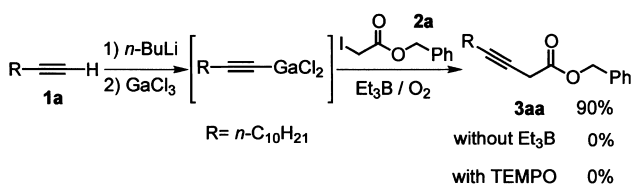
Treatment of terminal acetylenes with butyllithium, followed by an addition of gallium trichloride, afforded the corresponding alkynylgallium reagents. The reaction of the resulting alkynylgallium with α -halo carbonyl compounds in the presence of triethylborane as a radical initiator provided β,γ -acetylenic carbonyl compounds in good yields.

Very recently, organogallium reagents have attracted much attention and are widely used in organic synthesis.^{1–4} For instance, ethynylgallium generated from trimethylsilylethyne and gallium chloride causes ethenylation of silyl enol ethers.² Dichlorogallium hydride plays an important role in the radical reduction of alkyl halides.³ We have reported that allylgallium is an effective reagent for radical allylation of α -iodo or α -bromo carbonyl compounds (Scheme 1).^{4a} Here we wish to report a triethylborane-induced radical reaction of alkynylgalliums⁵ with α -iodo carbonyl compounds⁶ that provides β,γ -acetylenic carbonyl compounds.

Butyllithium (1.64 M hexane solution, 0.61 mL, 1.0 mmol) was added to an ethereal solution of 1-dodecyne (**1a**, 1.0 mmol) at 0 °C under argon atmosphere. After stirring for 20 min at the same temperature, GaCl₃ (1.0 M hexane solution, 1.0 mL, 1.0 mmol) was added to the resulting alkynyllithium. The reaction mixture was warmed to room temperature over a period of 30 min. Benzyl iodoacetate (**2a**, 138 mg, 0.5 mmol) and triethylborane⁷ (1.0 M hexane solution, 0.2 mL, 0.2 mmol) were added sequentially. Finally, air (5 mL) was introduced via a syringe, and the resulting mixture was stirred for an additional 2 h. Extractive workup followed by silica gel column purification provided benzyl 3-tetradecynoate (**3aa**) in 90% yield (Scheme 2).



Scheme 1.



Scheme 2.

Without triethylborane as a radical initiator, the reaction did not proceed at all. Moreover, in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), none of the expected products were detected in the reaction mixture. These results suggest that the reaction proceeds via a radical process. Typical examples of the reaction of 1-dodecynylgallium, generated from dodecynyllithium and GaCl₃, with various alkyl halides are listed in Table 1. Several characteristics of this reaction are noteworthy. (1) β,γ -Acetylenic carbonyl compounds **3** were obtained in moderate to good yields starting from a variety of α -iodo carbonyl compounds. Secondary iodo compounds such as **2b** and **2d** gave acetylenic products **3ab** and **3ad** in inferior yields compared to the corresponding primary iodides **2a** and **2c**. (2) An addition of benzyl iodoacetate to the alkynyllithium instead of an alkynylgallium gave no alkylation product. In this case, nucleophilic attack to the carbonyl group provided an α,β -acetylenic ketone and propargyl alcohol. Thus, the use of gallium chloride is essential for the formation of **3**. (3) Not only α -iodo carbonyl compounds but also α -iodoacetone nitrile afforded the corresponding adduct in good yield upon treatment with 1-dodecynylgallium reagent. (4) In the case of α -bromo carbonyl compounds such as α -bromoester **2h**, the reaction required longer reaction time compared to α -iodo compounds, and alkylation product **3aa** was obtained in moderate yield after stirring for 17 h. (5) The use of alkyl halides having no activating group such as 2-iodobutane or *t*-butyl iodide, resulted in the formation of negligible amounts of the desired adducts.

The reaction of various alkyl halides with alkynylgallium,⁵ prepared from ethynylbenzene **1b** or trimethylsilylethyne **1c**, was examined. The results are listed in Table 2. In all cases, alkylation products were obtained in higher yields than in the case of 1-dodecynylgallium reagent.

We propose the following reaction mechanism involving an iodine atom transfer process⁸ as depicted in Scheme 3. An ethyl radical, which is produced by the action of oxygen on triethylborane, abstracts the halogen atom from α -halo carbonyl compound to give an alkyl radical **4**. Then, the alkyl radical adds to the carbon-carbon triple bond of an alkynylgallium to

duced radical process. This method provides a useful tool for the synthesis of β,γ -acetylenic carbonyl compounds.

Experimental

^1H NMR and ^{13}C NMR spectra were taken on a Varian GEMINI 300 spectrometer in CDCl_3 as a solvent, and chemical shifts are given in δ value with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. Mass spectra were recorded on a JEOL JMS-700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layers of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF was freshly distilled from sodium benzophenone ketyl before use. Et_3B and GaCl_3 were purchased from Aldrich Chemicals and were diluted to prepare a 1.0 M hexane solution, which was stored under argon.

General Procedure for Alkynylation of α -Halo Carbonyl Compounds with Alkynylgallium. Butyllithium (0.61 mL, 1.64 M hexane solution, 1 M = 1 mol dm^{-3} , 1.0 mmol) was added dropwise to a solution of 1-dodecyne (**1a**, 166 mg, 1.0 mmol) in ether (2 mL). The resulting mixture was stirred for 20 min at 0 °C to prepare 1-dodecynyllithium. A solution of GaCl_3 (1.0 mL, 1.0 M hexane solution, 1.0 mmol) was introduced via a syringe. The reaction mixture was warmed to room temperature over a period of 30 min. Benzyl iodoacetate (**2a**, 138 mg, 0.50 mmol) and triethylborane (0.2 mL, 1.0 M hexane solution, 0.20 mmol) were sequentially added. After addition of air (5 mL) via a syringe, the mixture was stirred for another 2 h. The reaction mixture was poured into water and extracted with ethyl acetate (20 mL $\times$ 3). The combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuo. The residual oil was purified by silica-gel column chromatography to provide benzyl 3-tetradecynoate (**3aa**, 142 mg) in 90% yield.

Benzyl 3-Tetradecynoate (3aa): IR (neat) 3034, 2926, 2855, 1747, 1499, 1456, 1404, 1377, 1331, 1263, 1163, 980, 735, 696 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.88 (t, J = 6.6 Hz, 3H), 1.24–1.42 (m, 14H), 1.49 (tt, J = 7.2, 7.2 Hz, 2H), 2.19 (tt, J = 2.4, 7.2 Hz, 2H), 3.30 (t, J = 2.4 Hz, 2H), 5.17 (s, 2H), 7.26–7.40 (m, 5H); ^{13}C NMR (CDCl_3) δ 13.96, 18.65, 22.56, 26.01, 28.59, 28.76, 29.04, 29.21, 29.42, 29.48, 31.80, 67.00, 71.15, 84.09, 128.29, 128.39, 129.62, 135.68, 168.97. Found: C, 80.04; H, 9.85%. Calcd for $\text{C}_{21}\text{H}_{30}\text{O}_2$: C, 80.21; H, 9.62%.

Benzyl 2-Methyl-3-tetradecynoate (3ab): IR (neat) 3034, 2926, 2855, 1746, 1499, 1456, 1377, 1308, 1240, 1157, 1090, 735, 696 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.85 (t, J = 6.6 Hz, 3H), 1.20–1.38 (m, 14H), 1.40 (d, J = 7.2 Hz, 3H), 1.40–1.54 (m, 2H), 2.15 (dt, J = 2.4, 6.9 Hz, 2H), 3.40 (dq, J = 2.4, 7.2 Hz, 1H), 5.15 (s, 2H), 7.26–7.42 (m, 5H); ^{13}C NMR (CDCl_3) δ 14.09, 18.39, 18.72, 22.67, 28.71, 28.80, 29.12, 29.31, 29.50, 29.7, 31.88, 32.37, 66.80, 77.38, 83.18, 127.92, 128.15, 128.48, 135.80, 171.87. HRMS m/z calcd for $\text{C}_{22}\text{H}_{32}\text{O}_2$ 328.2402, found 328.2397.

N-Benzyl-3-tetradecynamide (3ac): IR (nujol) 3294, 1641, 1549, 1414, 1246, 1067, 750, 698, 592 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.88 (t, J = 6.6 Hz, 3H), 1.20–1.40 (m, 14H), 1.46 (tt, J = 7.2, 7.2 Hz, 2H), 2.17 (tt, J = 2.4, 7.2 Hz, 2H), 3.23 (t, J = 2.4 Hz, 2H), 4.49 (s, 1H), 4.67 (s, 1H), 6.87 (bs, 1H), 7.26–7.40 (m, 5H);

^{13}C NMR (CDCl_3) δ 13.92, 18.55, 22.52, 27.68, 28.49, 28.75, 28.94, 29.16, 29.34, 29.43, 31.76, 43.59, 73.00, 85.56, 127.58, 127.61, 128.77, 138.02, 167.54. HRMS m/z calcd for $\text{C}_{21}\text{H}_{31}\text{NO}$ 313.2406, found 313.2393.

N-Benzyl-2-methyl-3-tetradecynamide (3ad): IR (neat) 3308, 3065, 2926, 2855, 1661, 1524, 1497, 1454, 1362, 1331, 1231, 1078, 1030, 729, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.88 (t, J = 6.6 Hz, 3H), 1.20–1.38 (m, 14H), 1.40–1.50 (m, 2H), 1.45 (d, J = 7.2 Hz, 3H), 2.17 (dt, J = 2.4, 7.2 Hz, 2H), 3.29 (dq, J = 2.4, 7.2 Hz, 1H), 4.46 (d, J = 5.7 Hz, 2H), 6.89 (bs, 1H), 7.26–7.40 (m, 5H); ^{13}C NMR (CDCl_3) δ 14.10, 18.68, 19.11, 22.66, 28.65, 28.85, 29.06, 29.29, 29.47, 29.55, 31.88, 33.80, 43.67, 78.82, 86.14, 127.46, 127.49, 128.70, 138.10, 171.25. HRMS m/z calcd for $\text{C}_{22}\text{H}_{33}\text{NO}$ 327.2562, found 327.2555.

Ethyl 3-Tetradecynoate (3ae): IR (neat) 2926, 2855, 1747, 1466, 1369, 1259, 1178, 1032, 935, 721 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.85 (d, J = 6.9 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.20–1.40 (m, 14H), 1.46 (tt, J = 6.9, 6.9 Hz, 2H), 2.16 (tt, J = 2.4, 6.9 Hz, 2H), 3.21 (t, J = 2.4 Hz, 2H), 4.16 (q, J = 7.2 Hz, 2H); ^{13}C NMR (CDCl_3) δ 13.96, 13.99, 18.66, 22.56, 26.01, 28.61, 28.76, 29.05, 29.21, 29.43, 29.48, 31.80, 61.33, 71.40, 83.89, 169.14. HRMS m/z calcd for $\text{C}_{16}\text{H}_{28}\text{O}_2$ 252.2089, found 252.2077.

(E)-2-Hexenyl 3-Tetradecynoate (3af): IR (neat) 2926, 2856, 1749, 1460, 1379, 1329, 1259, 1167, 972 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.84 (t, J = 7.2 Hz, 3H), 0.86 (t, J = 7.2 Hz, 3H), 1.16–1.52 (m, 18H), 1.99 (dt, J = 7.2, 7.2 Hz, 2H), 2.15 (t, J = 6.9 Hz, 2H), 3.21 (s, 2H), 4.52 (d, J = 6.3 Hz, 2H), 5.52 (dt, J = 15.3, 6.3 Hz, 1H), 5.75 (dt, J = 15.3, 6.9 Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.41, 13.90, 18.63, 21.87, 22.52, 25.96, 28.58, 28.73, 29.02, 29.18, 29.40, 29.45, 31.77, 34.17, 66.02, 71.31, 83.86, 123.63, 136.76, 168.84. HRMS m/z calcd for $\text{C}_{20}\text{H}_{34}\text{O}_2$ 304.2559, found 304.2561.

3-Tetradecynenitrile (3ag): IR (neat) 2926, 2855, 2260, 2241, 1466, 1408, 1377, 1315, 914, 721 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.85 (t, J = 6.6 Hz, 3H), 1.20–1.36 (m, 14H), 1.46 (tt, J = 7.2, 7.2 Hz, 2H), 2.13 (tt, J = 2.4, 7.2 Hz, 2H), 3.29 (t, J = 2.4 Hz, 2H); ^{13}C NMR (CDCl_3) δ 9.11, 13.95, 18.38, 22.55, 28.14, 28.71, 28.97, 29.19, 29.38, 29.45, 31.78, 66.56, 84.66, 115.09. This compound was unstable for elemental analysis.

Benzyl 4-Phenyl-3-butyrate (3ba): IR (nujol) 2345, 1740, 1340, 1263, 1196, 914, 754, 743, 702, 691 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.56 (s, 2H), 5.22 (s, 2H), 7.26–7.50 (m, 10H); ^{13}C NMR (CDCl_3) δ 26.57, 67.20, 80.98, 83.64, 123.03, 128.27, 128.28, 128.31, 128.46, 128.67, 131.82, 135.57, 168.17. Found: C, 81.61; H, 5.70%. Calcd for $\text{C}_{17}\text{H}_{14}\text{O}_2$: C, 81.58; H, 5.64%.

Benzyl 2-Methyl-4-phenyl-3-butyrate (3bb): IR (neat) 3034, 2990, 2941, 1744, 1599, 1491, 1454, 1379, 1171, 1097, 1022, 961, 907, 756, 692 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.55 (d, J = 7.2 Hz, 3H), 3.69 (q, J = 7.2 Hz, 1H), 5.23 (s, 2H), 7.28–7.44 (m, 10H); ^{13}C NMR (CDCl_3) δ 17.91, 32.89, 66.98, 82.82, 86.97, 123.13, 128.02, 128.18, 128.26, 128.31, 128.63, 131.80, 135.86, 171.30. Found: C, 81.56; H, 6.26%. Calcd for $\text{C}_{18}\text{H}_{16}\text{O}_2$: C, 81.79; H, 6.10%.

N-Benzyl-4-phenyl-3-butyramide (3bc): IR (nujol) 3279, 1647, 1549, 1491, 1236, 1070, 1011, 758, 739, 691 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.48 (s, 2H), 4.50 (d, J = 6.3 Hz, 2H), 6.83 (bs, 1H), 7.24–7.40 (m, 10H); ^{13}C NMR (CDCl_3) δ 28.28, 43.73, 82.20, 85.92, 122.39, 127.67, 127.68, 128.47, 128.70, 128.85, 131.75, 137.98, 166.78. HRMS m/z calcd for $\text{C}_{17}\text{H}_{15}\text{NO}$ 249.1154, found 254.1164.

N-Benzyl-2-methyl-4-phenyl-3-butyramide (3bd): IR

(neat) 3298, 2345, 1649, 1491, 1377, 1227, 1078, 1030, 986, 763, 745, 694 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.59 (d, $J = 7.5$ Hz, 3H), 3.56 (q, $J = 7.5$ Hz, 1H), 4.50 (d, $J = 6.0$ Hz, 2H), 6.95 (bs, 1H), 7.24–7.46 (m, 10H); ^{13}C NMR (CDCl_3) δ 18.64, 34.15, 43.64, 85.31, 87.73, 122.29, 127.39, 127.41, 128.26, 128.41, 128.63, 131.53, 137.97, 170.46. HRMS m/z calcd for $\text{C}_{18}\text{H}_{17}\text{NO}$ 263.1310, found 263.1315.

Benzyl 4-Trimethylsilyl-3-butynoate (3ca): IR (neat) 3036, 2961, 2187, 1747, 1499, 1456, 1400, 1377, 1332, 1252, 1161, 1051, 845, 760, 737, 698, 646 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.16 (s, 9H), 3.35 (s, 2H), 5.16 (s, 2H), 7.30–7.40 (m, 5H); ^{13}C NMR (CDCl_3) δ –0.32, 27.07, 67.06, 88.58, 97.23, 128.15, 128.40, 128.62, 135.58, 167.84. Found: C, 68.45; H, 7.56%. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{Si}$: C, 68.25; H, 7.36%.

Benzyl 2-Methyl-4-trimethylsilyl-3-butynoate (3cb): IR (neat) 2960, 2176, 1746, 1499, 1456, 1379, 1250, 1173, 1119, 1090, 1030, 966, 845, 760, 735, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ –0.14 (s, 9H), 1.42 (d, $J = 7.2$ Hz, 3H), 3.46 (q, $J = 7.2$ Hz, 1H), 5.15 (s, 1H), 5.18 (s, 1H), 7.28–7.38 (m, 5H); ^{13}C NMR (CDCl_3) δ –0.23, 17.80, 33.18, 66.84, 87.21, 103.36, 127.86, 128.25, 128.59, 135.89, 171.05. Found: C, 68.96; H, 7.62%. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2\text{Si}$: C, 69.19; H, 7.74%.

N-Benzyl 4-Trimethylsilyl-3-butyramide (3cc): IR (neat) 3292, 2959, 2181, 1659, 1535, 1454, 1250, 1030, 845, 760, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.13 (s, 9H), 3.28 (s, 2H), 4.47 (d, $J = 6.0$ Hz, 2H), 6.84 (bs, 1H), 7.24–7.40 (m, 5H); ^{13}C NMR (CDCl_3) δ –0.32, 28.74, 43.74, 91.32, 99.33, 127.45, 127.56, 128.72, 137.62, 166.19. Found: C, 68.27; H, 7.62%. Calcd for $\text{C}_{14}\text{H}_{19}\text{NOSi}$: C, 68.52; H, 7.80%.

N-Benzyl 2-Methyl-4-trimethylsilyl-3-butyramide (3cd): IR (neat) 3298, 2961, 2172, 1661, 1528, 1454, 1250, 1121, 1030, 928, 845, 760, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.12 (s, 9H), 1.47 (d, $J = 7.2$ Hz, 3H), 3.32 (q, $J = 7.2$ Hz, 1H), 4.45 (d, $J = 6.0$ Hz, 2H), 6.88 (bs, 1H), 7.24–7.40 (m, 5H); ^{13}C NMR (CDCl_3) δ –0.22, 18.43, 34.55, 43.79, 90.34, 105.14, 127.43, 127.53, 128.72, 137.84, 170.08. HRMS m/z calcd for $\text{C}_{15}\text{H}_{21}\text{NOSi}$ 259.1392, found 259.1380.

4-Methyl-3-oxa-5-hexadecyne (8): IR (nujol) 2928, 2856, 2239, 1466, 1369, 1329, 1313, 1240, 1173, 1130, 1101, 937, 845, 721 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.85 (t, $J = 6.9$ Hz, 3H), 1.19 (t, $J = 6.9$ Hz, 3H), 1.18–1.40 (m, 14H), 1.37 (d, $J = 6.6$ Hz, 3H), 1.42–1.54 (m, 2H), 2.17 (dt, $J = 1.8, 7.2$ Hz, 2H), 3.39 (dq, $J = 7.2, 6.9$ Hz, 1H), 3.73 (dq, $J = 7.2, 6.9$ Hz, 1H), 4.11 (dq, $J = 1.8, 6.9$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 14.10, 15.20, 18.66, 22.58, 22.67, 28.71, 28.82, 29.10, 29.31, 29.52, 29.56, 31.89, 63.80, 65.22, 80.26, 85.25. HRMS m/z calcd for $\text{C}_{16}\text{H}_{30}\text{O}$ 238.2297, found 238.2301.

This work was supported by Grants-in-Aids for Scientific Research (Nos. 12305058 and 10208208) from the Ministry of Education, Culture, Sports, Science and Technology. H. Y. acknowledges JSPS for financial support. H. S. also thanks Banyu Pharmaceutical Co., Ltd.

References

- a) Y. Kido, M. Arisawa, and M. Yamaguchi, *J. Syn. Org. Chem., Jpn.*, **2000**, 1030, and references herein. b) S. Araki, T. Horie, M. Kato, T. Hirashita, H. Yamamura, and M. Kawai, *Tetrahedron Lett.*, **40**, 2331 (1999). c) Y. Han, Z. Chi, and Y.-Z. Huang, *Synth. Commun.*, **29**, 1287 (1999). d) F. Yonehara, Y. Kido, S. Morita, and M. Yamaguchi, *J. Am. Chem. Soc.*, **123**, 11310 (2001). e) T. Tsuji, S. Usugi, H. Yorimitsu, H. Shinokubo, S. Matsubara, and K. Oshima, *Chem. Lett.*, **2002**, 2. f) K. Takai, Y. Ikawa, K. Ishii, and M. Kumanda, *Chem. Lett.*, **2002**, 172. g) T. Ooi, J. Morikawa, H. Ichikawa, and K. Maruoka, *Tetrahedron Lett.*, **40**, 5881 (1999).
- a) M. Yamaguchi, T. Tsukagoshi, and M. Arisawa, *J. Am. Chem. Soc.*, **121**, 4074 (1999). b) M. Arisawa, K. Akamatsu, and M. Yamaguchi, *Org. Lett.*, **3**, 789 (2001). c) M. Arisawa, C. Miyagawa, S. Yoshimura, Y. Kido, and M. Yamaguchi, *Chem. Lett.*, **2001**, 1080.
- S. Mikami, K. Fujita, T. Nakamura, H. Yorimitsu, H. Shinokubo, S. Matsubara, and K. Oshima, *Org. Lett.*, **3**, 1855 (2001).
- a) S. Usugi, H. Yorimitsu, and K. Oshima, *Tetrahedron Lett.*, **42**, 4535 (2001). b) S. Usugi, T. Tsuritani, H. Yorimitsu, H. Shinokubo, and K. Oshima, *Bull. Chem. Soc. Jpn.*, **75**, 841 (2002).
- a) A. L. Dalch, L. Latos-Grazynski, B. C. Noll, and S. L. Phillips, *Inorg. Chem.*, **32**, 1124 (1993). b) K. E. Lee and K. T. Higa, *J. Organomet. Chem.*, **449**, 53 (1993). c) K. M. Kadish, J.-L. Cornillon, A. Coutsolelos, and R. Guillard, *Inorg. Chem.*, **26**, 4167 (1987).
- Et_3B -catalyzed radical reactions with α -halo carbonyl compounds, see: a) T. Nakamura, H. Yorimitsu, H. Shinokubo, and K. Oshima, *Synlett*, **1998**, 1351. b) H. Yorimitsu, K. Wakabayashi, H. Shinokubo, and K. Oshima, *Bull. Chem. Soc. Jpn.*, **74**, 1963 (2001). c) H. Yorimitsu, T. Nakamura, H. Shinokubo, K. Oshima, K. Omoto, and H. Fujimoto, *J. Am. Chem. Soc.*, **122**, 11041 (2000).
- For triethylborane as a radical initiator, see: a) K. Nozaki, K. Oshima, and K. Utimoto, *J. Am. Chem. Soc.*, **109**, 2547 (1987). b) K. Oshima and K. Utimoto, *J. Syn. Org. Chem., Jpn.*, **1989**, 40. c) H. Yorimitsu and K. Oshima, "Radicals in Organic Synthesis," ed by P. Renaud and M. P. Sibi, WILEY-VCH, Weinheim (2001), Vol. 1, Chap. 1.2.
- For atom-transfer radical reactions, see: a) D. P. Curran, *Synthesis*, **1988**, 417. b) D. P. Curran, M.-H. Chen, and D. Kim, *J. Am. Chem. Soc.*, **108**, 2498 (1986). c) D. P. Curran and C.-T. Chang, *Tetrahedron Lett.*, **28**, 2477 (1987). d) J. Byers, "Radicals in Organic Synthesis," ed by P. Renaud and M. P. Sibi, WILEY-VCH, Weinheim (2001), Vol. 1, Chap. 1.5.
- a) J. Gong and P. L. Fuchs, *J. Am. Chem. Soc.*, **118**, 4486 (1996). b) J. S. Xiang and P. L. Fuchs, *Tetrahedron Lett.*, **37**, 5269 (1996). c) J. S. Xiang, W. Jiang, and P. L. Fuchs, *Tetrahedron Lett.*, **38**, 6635 (1997).