

Triethylborane Induced Radical Reaction of Gallium Enolates with α-Halo Esters

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 March 19, 2002)

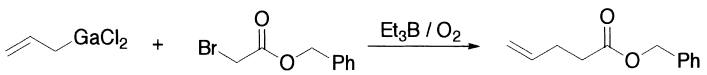
Treatment of silyl enolates with methyllithium followed by an addition of gallium trichloride afforded the corresponding gallium enolates. The reaction of the resulting gallium enolates with α-halo carbonyl compounds in the presence of triethylborane as a radical initiator provided 1,4-dicarbonyl compounds in good yields.

We have recently reported that allylgallium is an effective reagent for radical allylation of α-iodo or α-bromo carbonyl compounds.[1] For instance, treatment of benzyl bromoacetate with allylgallium, prepared from allylmagnesium chloride and gallium trichloride, in the presence of triethylborane[2] as a radical initiator in THF provided benzyl 4-pentenoate in good yield (Scheme 1). Here we wish to report a triethylborane-induced radical reaction of gallium enolates[3] with α-haloesters[4] providing γ-keto esters.[5]

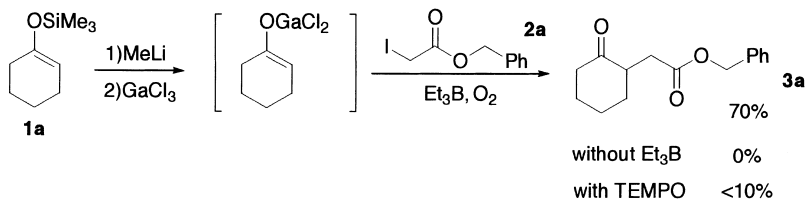
Methyllithium (1.04 M ether solution, 1.01 mL, 1.05 mmol) was added to a solution of 1-trimethylsiloxy-1-cyclohexene (**1a**) in ether at 0 °C under argon atmosphere.[6] After stirring for 30 min at the same temperature, $GaCl_3$ (1.0 M hexane solution, 1.0 mL, 1.0 mmol) was added to the resulting lithium enolate. The reaction mixture was warmed to room temperature over a period of 30 min. Benzyl iodoacetate (**2a**, 0.5 mmol) and Et_3B (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 3 h. Extractive workup followed by silica gel column purification provided benzyl (2-oxocyclohexyl)acetate (**3a**) in 70% yield (Scheme 2).

Without Et_3B as a radical initiator, the reaction did not proceed at all. Moreover, in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl), none of expected products were detected in the reaction mixture. These results suggest that the reaction proceeds via a radical process. The results of the reaction of benzyl iodoacetate (**2a**) with various gallium enolates, generated from the corresponding silyl enolates in situ, are listed in Table 1. Several characteristics of this reaction are noteworthy. (1) γ-Keto esters were obtained in good yields starting from a variety of silyl enolates. (2) In the case of silyl enolate **1g**, prepared from cyclopropyl methyl ketone, benzyl 7-iodo-4-oxo-heptanoate (**3g**) was obtained exclusively via cyclopropane ring cleavage (entry 6). (3) An addition of benzyl iodoacetate to the lithium enolate instead of the gallium enolate provided a complex mixture. (4) Only a trace amount of the product was obtained from the reaction of the gallium enolate derived from **1d** (entry 3). In this case, the benzyl radical ($^{\bullet}C(Ph)(OGaCl_2)CH_2CH_2COOCH_2Ph$), which resulted from the addition of α-carbonyl radical ($^{\bullet}CH_2COOCH_2Ph$) to the gallium enolate, would be unreactive due to stabilization by the phenyl group.

Next, the reaction of various α-halo carbonyl compounds with the gallium enolate prepared from **1a** was examined (Table 2). Not only primary α-iodo ester **2a** but also primary α-bromo ester **2b**, α-iodo amide **2d**, and α-iodo nitrile **2f** afforded the corresponding adducts in good yields upon treat-

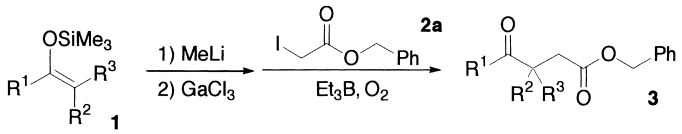


Scheme 1.



Scheme 2.

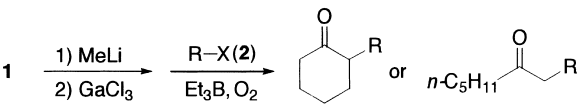
Table 1. Reaction of Gallium Enolates with Benzyl Iodoacetate

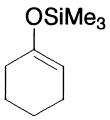
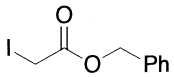
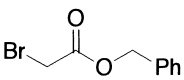
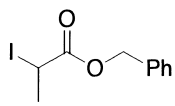
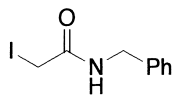
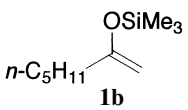


Entry		R^1	R^2	R^3	Time/h	Product	Yield/%
1	**1b**	n-C_5H_{11}	H	H	6	**3b**	76
2	**1c**	t-Bu	H	H	2	**3c**	50
3	**1d**	Ph	H	H	7	**3d**	trace
4	**1e**[a]	Pr	Et(H)	H(Et)	3	**3e**	66
5	**1f**	i-Pr	Me	Me	10	**3f**	26
6	**1g**		H	H	9	**3g**	60[b]

a) A mixture of (*E*) and (*Z*)-stereoisomer
b) Product was $ICH_2CH_2CH_2C(O)CH_2CH_2C(O)OCH_2Ph$

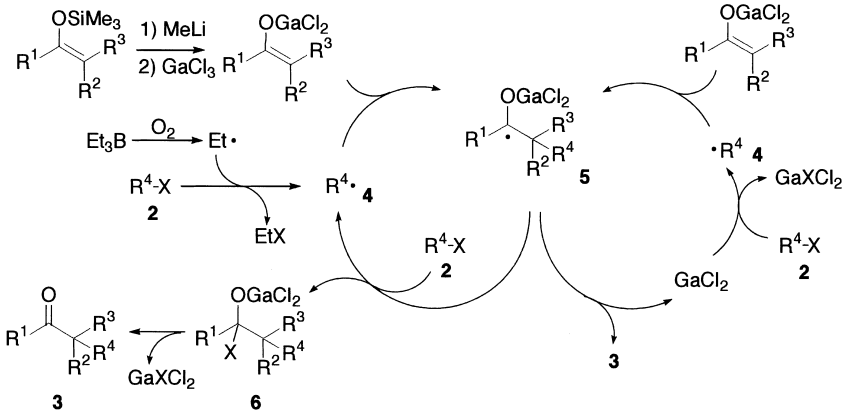
Table 2.



Entry	Substrate	R–X		Time/h	Product	Yield/%
1	 **1a**		**2a**	3	**3a**	70
2			**2b**	4	**3a**	69
3			**2c**	12	**3h**	7 (50/50)
4			**2d**	4	**3i**	51
5			**2e**	9	**3j**	17
6			**2f**	4	**3k**	76
7	 **1b**	**2c**		4	**3l**	49
8		**2d**		3	**3m**	45
9		**2e**		5	**3n**	37
10		**2f**		4	**3o**	77

ment with gallium enolates. In contrast, the reaction of secondary α-iodo ester **2c** and α-iodo ketone **2e** provided the desired products in only low yields. The use of alkyl halides without an activating group, such as isopropyl iodide or t-butyl iodide, resulted in the formation of a negligible amount of the expected adducts.

We propose the reaction mechanism involving an iodine atom transfer process that is depicted in Scheme 3. An ethyl radical, which is produced by the action of oxygen on triethylborane, abstracts the halogen atom from an α-halo carbonyl compound **2** (R^4-X) to give the alkyl radical **4** (R^4·). Next, the alkyl radical **4** adds to the carbon-carbon double bond of a gallium enolate to give the alkyl radical **5**. The radical **5** then reacts with **2** to yield the adduct **6** and regenerates the alkyl radical **4**.[7] The adduct **6** eventually eliminates gallium halide to furnish the product **3**. Elimination of gallium(II) chloride from



Scheme 3.

the alkyl radical **5** to afford **3** directly is an alternative pathway. The resulting gallium(II) species abstracts halogen from **2** to regenerate the alkyl radical **4**, and the radical chain reaction continues.[8]

In conclusion, we have developed an alkylation reaction of various gallium enolates via a triethylborane-induced radical process. An addition of radicals to silyl enolates is limited to polyhalogenated radicals such as perfluoroalkyl or trichloromethyl radicals. Conversion of silyl enolates to gallium enolates enhances the reactivity of the enol moiety toward radicals, and allows us to employ carbonyl- and cyano-substituted alkyl radicals.

Experimental

^{1}H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) 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 layer of Merck Silica gel $60F_{254}$. 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 was purchased from Aldrich Chemicals and was diluted to prepare a 1.0 M hexane solution, which was stored under argon.

General Procedure for the Reaction of Gallium Enolates with α-Halo Carbonyl Compounds. To a solution of 1-trimethylsiloxy-1-cyclohexene (170 mg, 1.0 mmol) in ether (2 mL), methyllithium (1.04 M ether solution, 1 M = 1 mol dm^{-3}, 1.01 mL, 1.05 mmol) was added dropwise via a syringe at 0 °C. After the mixture was stirred for 30 min, gallium trichloride (1.0 mL, 1.0 M hexane solution, 1.0 mmol) was dropped at 0 °C. The mixture was allowed to warm to room temperature over a period of 30 min, and then benzyl iodoacetate (138 mg, 0.5 mmol) and Et_3B (1.0 M hexane solution, 0.20 mL, 0.20 mmol) were added sequentially. Finally, air (5 mL) was introduced via a syringe, and the resulting mixture was stirred for 3 h at 25 °C. The mixture was then poured into water and extracted with ethyl acetate (20 mL × 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 (2-oxocyclohexyl)acetate (**3a**, 86 mg) in 70% yield.

Benzyl (2-Oxocyclohexyl)acetate (3a) IR (neat) 2937, 2862, 1736, 1711, 1499, 1450, 1389, 1350, 1312, 1275, 1213, 1163, 1132, 978, 740, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30–1.46 (m, 1H), 1.50–1.78 (m, 2H), 1.80–1.90 (m, 1H), 2.00–2.26 (m, 3H), 2.26–2.46 (m, 2H), 2.76–2.92 (m, 2H), 5.10 (s, 2H), 7.24–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.00, 27.57, 33.68, 34.27, 41.63, 46.95, 66.13, 128.08, 128.12, 128.51, 136.07, 172.44, 210.89. Found: C, 73.32; H, 7.45%. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37%.

Benzyl 4-Oxononanoate (3b) IR (neat) 2932, 2860, 1736, 1717, 1499, 1456, 1410, 1354, 1163, 1080, 1003, 739, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.2 Hz, 3H), 1.16–1.36 (m, 4H), 1.56 (tt, J = 7.5, 7.5 Hz, 2H), 2.41 (t, J = 6.0 Hz, 2H), 2.61 (t, J = 6.0 Hz, 2H), 2.71 (t, J = 6.0 Hz, 2H), 5.09 (s, 2H), 7.28–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.74, 22.29, 23.35, 27.89, 31.25, 36.88, 42.68, 66.40, 128.23, 128.27, 128.60, 135.98, 172.79, 209.18. Found: C, 73.46; H, 8.65%. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45%.

Benzyl 5,5-Dimethyl-4-oxohexanoate (3c) IR (neat) 3034, 2970, 2935, 2874, 1738, 1707, 1499, 1479, 1456, 1384, 1350, 1315, 1161, 1086, 978, 739, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 9H), 2.63 (t, J = 6.6 Hz, 2H), 2.83 (t, J = 6.6 Hz, 2H), 5.12 (s, 2H), 7.30–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 26.39, 28.08, 31.34, 43.83, 66.34, 128.25, 128.26, 128.59, 136.02, 172.96, 214.12. Found: C, 72.71; H, 8.20%. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%.

Benzyl 3-Ethyl-4-oxoheptanoate (3e) IR (neat) 3034, 2964, 2936, 2878, 1736, 1713, 1499, 1456, 1407, 1385, 1354, 1329, 1228, 1175, 957, 750, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.9 Hz, 3H), 0.89 (t, J = 6.9 Hz, 3H), 1.36–1.72 (m, 4H), 2.37 (dd, J = 3.9, 16.5 Hz, 1H), 2.48 (t, J = 7.2 Hz, 2H), 2.82 (dd, J = 9.9, 16.5 Hz, 1H), 2.88–2.98 (m, 1H), 5.07 (s, 1H), 5.09 (s, 1H), 7.28–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 11.15, 13.57, 16.72, 24.35, 34.68, 44.22, 48.42, 66.37, 128.29, 128.30, 128.61, 135.90, 172.53, 212.86. Found: C, 73.04; H, 8.58%. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45%.

Benzyl 3,3,5-Trimethyl-4-oxohexanoate (3f) IR (neat) 2972, 2936, 2874, 1738, 1705, 1499, 1462, 1381, 1346, 1177, 1128, 1028, 1003, 741, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.06 (d, J = 6.6 Hz, 6H), 1.27 (s, 6H), 2.62 (s, 2H), 3.10 (sept, J = 6.6 Hz, 1H), 5.08 (s, 2H), 7.30–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.80, 24.60, 34.39, 43.72, 46.26, 66.15, 128.26, 128.35, 128.59, 135.97,

171.61, 218.42. Found: C, 73.44; H, 8.62%. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45%.

Benzyl 7-Iodo-4-oxoheptanate (3g) IR (neat) 3032, 2957, 1736, 1717, 1499, 1454, 1408, 1354, 1202, 1169, 1094, 1003, 752, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.05 (tt, J = 6.6, 6.9 Hz, 2H), 2.58 (t, J = 6.9 Hz, 2H), 2.63 (t, J = 6.3 Hz, 2H), 2.72 (t, J = 6.3 Hz, 2H), 3.17 (t, J = 6.6 Hz, 2H), 5.09 (s, 2H), 7.28–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 6.06, 26.96, 27.87, 37.10, 42.86, 66.48, 128.26, 128.32, 128.62, 135.87, 172.58, 207.41. This compound was unstable and we could not obtain an analytically pure sample.

Benzyl 2-(2-Oxocyclohexyl)propanoate (3h) IR (neat) 2939, 2864, 1736, 1711, 1499, 1454, 1381, 1155, 1042, 739, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (d, J = 7.2 Hz, 3H), 1.48–1.72 (m, 3H), 1.82–2.06 (m, 3H), 2.20–2.42 (m, 2H), 2.58–2.68 (m, 1H), 2.70–2.90 (m, 1H), 5.09 (s, 2H), 7.26–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.52, 24.83, 27.45, 30.98, 39.25, 42.06, 63.21, 66.10, 128.13, 128.17, 128.56, 136.20, 175.22, 210.87. HRMS *m/z* calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1412.

***N*-Benzyl-2-(2-oxocyclohexyl)ethanamide (3i)** IR (nujol) 3298, 1697, 1639, 1556, 1348, 1312, 1286, 1236, 1132, 1080, 1018, 741, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–1.42 (m, 1H), 1.48–1.78 (m, 2H), 1.78–1.90 (m, 1H), 2.00–2.22 (m, 3H), 2.26–2.42 (m, 2H), 2.58–2.68 (m, 1H), 2.86–3.00 (m, 1H), 4.38 (d, J = 5.8 Hz, 1H), 4.39 (d, J = 5.8 Hz, 1H), 6.53 (bs, 1H), 7.20–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.05, 27.79, 34.32, 36.49, 41.86, 43.48, 47.66, 127.38, 127.64, 128.64, 138.20, 172.31, 212.76. HRMS *m/z* calcd for $C_{15}H_{19}NO_2$ 245.1416, found 245.1415.

Benzyl 2-Methyl-4-oxononanoate (3l) IR (neat) 3067, 3034, 2934, 2874, 1736, 1717, 1499, 1456, 1408, 1379, 1259, 1165, 1138, 1030, 970, 910, 750, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 7.2 Hz, 3H), 1.17 (d, J = 7.2 Hz, 3H), 1.12–1.32 (m, 4H), 1.53 (tt, J = 7.5, 7.2 Hz, 2H), 2.36 (t, J = 7.5 Hz, 2H), 2.43 (dd, J = 17.1, 5.1 Hz, 1H), 2.87 (dd, J = 17.1, 8.1 Hz, 1H), 2.99 (m, 1H), 5.08 (s, 1H), 5.10 (s, 1H), 7.26–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.76, 16.95, 22.30, 23.29, 31.26, 34.66, 42.88, 45.61, 66.33, 128.10, 128.19, 128.59, 136.16, 175.76, 209.14. Found: C, 73.73; H, 8.85%. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75%.

***N*-Benzyl-4-oxononanamide (3m)** IR (nujol) 3314, 1701, 1639, 1551, 1412, 1236, 1030, 723, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.2 Hz, 3H), 1.16–1.36 (m, 4H), 1.54 (tt, J = 7.2, 7.2 Hz, 2H), 2.40 (t, J = 7.2 Hz, 2H), 2.44 (t, J = 6.6 Hz, 2H), 2.75 (t, J = 6.6 Hz, 2H), 4.36 (s, 1H), 4.38 (s, 1H), 6.36 (bs, 1H), 7.20–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.68, 22.22, 23.31, 29.67, 31.17, 37.49, 42.63, 43.44, 127.37, 127.86, 128.62, 138.31, 172.15, 210.53. HRMS *m/z* calcd for $C_{16}H_{23}NO_2$ 261.1729, found 261.1734.

1-Phenylnona-1,4-dione (3n) IR (neat) 2932, 2860, 1713, 1688, 1597, 1582, 1448, 1400, 1358, 1238, 1211, 1180, 1126, 1003, 754, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 6.9 Hz, 3H), 1.20–1.38 (m, 4H), 1.60 (tt, J = 7.2, 7.5 Hz, 2H), 2.50 (t, J = 7.5 Hz, 2H), 2.83 (t, J = 6.3 Hz, 2H), 3.26 (t, J = 6.3 Hz, 2H), 7.40–7.46 (m, 2H), 7.50–7.58 (m, 1H), 7.92–8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.77, 22.33, 23.45, 31.31, 32.27, 36.10, 42.90, 128.11, 128.62, 133.16, 136.84, 198.87, 209.93. HRMS *m/z* calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1454.

4-Oxononanenitrile (3o) IR (neat) 2959, 2934, 2862, 2249, 1717, 1468, 1414, 1377, 1128, 1082 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 6.9 Hz, 3H), 1.16–1.36 (m, 4H), 1.57 (tt, J = 7.5, 7.5 Hz, 2H), 2.41 (t, J = 7.5 Hz, 2H), 2.55 (t, J = 7.2 Hz, 2H), 2.76 (t, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.20, 13.68, 22.22, 23.23, 31.13, 37.55, 42.37, 119.08, 206.49. Found: C, 70.60; H, 9.85%. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87%.

Compounds **3j**[9] and **3k**[5a] are found in the literature.

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

1 a) S. Usugi, H. Yorimitsu, and K. Oshima, *Tetrahedron Lett.*, **42**, 4535 (2001). b) S. Usugi, H. Yorimitsu, H. Shinokubo, and K. Oshima, *Bull. Chem. Soc. Jpn.*, **43**, 841 (2002).

2 For triethylborane as a radical initiator, see: a) K. Nozaki, K. Oshima, and K. Utimoto, *J. Am. Chem. Soc.*, **109**, 2547 (1987). b) K. Nozaki, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **39**, 923 (1989). c) K. Oshima and K. Utimoto, *J. Syn. Org. Chem., Jpn.*, **47**, 40 (1989). d) 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, p. 11. e) C. Ollivier and P. Renaud, *Chem. Rev.*, **101**, 3415 (2001).

3 For reactions involving gallium enolates, see: a) M. Yamaguchi, T. Tsukagoshi, and M. Arisawa, *J. Am. Chem. Soc.*, **121**, 4074 (1999). b) Y. Han and Y. Z. Huang, *Tetrahedron Lett.*, **39**, 7751 (1998).

4 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).

5 For radical reactions of metal enolates, see: a) K. Miura, N. Fujisawa, H. Saito, D. Wang, and A. Hosomi, *Org. Lett.*, **3**, 4055 (2001). b) G. A. Russell and L. L. Herold, *J. Org. Chem.*, **50**, 1037 (1985). c) Y. Watanabe, T. Yoneda, Y. Ueno, and T. Toru, *Tetrahedron Lett.*, **31**, 6669 (1990). d) K. Miura, M. Taniguchi, K. Nozaki, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **31**, 6391 (1990). e) K. Miura, Y. Takeyama, K. Oshima, and K. Utimoto, *Bull. Chem. Soc. Jpn.*, **64**, 1542 (1991). f) J. Sugimoto, K. Miura, K. Oshima, and K. Utimoto, *Chem. Lett.*, **1991**, 1319. g) K. Miura, J. Sugimoto, K. Oshima, and K. Utimoto, *Bull. Chem. Soc. Jpn.*, **65**, 1513. h) S. Tanaka, T. Nakamura, H. Yorimitsu, H. Shinokubo, and K. Oshima, *Org. Lett.*, **2**, 1911 (2000). i) T. Nakamura, S. Tanaka, H. Yorimitsu, H. Shinokubo, and K. Oshima, *Computes Rendus Acad. Sci. Paris, Chim.*, **4**, 461 (2001).

6 C. H. Heathcock, C. T. Buse, W. A. Kleschick, M. C. Pirrung, J. E. Sohn, and J. Lampe, *J. Org. Chem.*, **45**, 1066 (1980).

7 For atom-transfer radical reactions, see. a) D. P. Curran, *Synthesis*, **1988**, 417; D. P. Curran, M.-H. Chen, and D. Kim, *J. Am. Chem. Soc.*, **108**, 2498 (1986). b) D. P. Curran and C.-T. Chang, *Tetrahedron Lett.*, **28**, 2477 (1987). c) J. Byers, "Radicals in Organic Synthesis," ed by P. Renaud and M. P. Sibi, WILEY-VCH, Weinheim (2001), Vol. 1, Chap. 1.5, p. 72.

8 Gallium(II) species has been proposed to be involved in a $HGaCl_2$-mediated radical reduction reaction, see: S. Mikami, K. Fujita, T. Nakamura, H. Yorimitsu, H. Shinokubo, S. Matsubara, and K. Oshima, *Org. Lett.*, **3**, 1853 (2001).

9 M. Yasuda, T. Oh-hata, I. Shibata, A. Baba, and H. Matsuda, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 859.