Isomerization Reaction of Olefin Using $RuClH(CO)(PPh_3)_3$

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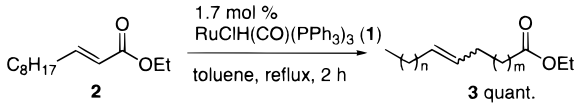
When methyl 5-(*tert*-butyldiphenylsilyl)oxy-2-pentenoate was refluxed in toluene in the presence of $RuClH(CO)(PPh_3)_3$ (5 mol %), double-bond migration took place to afford methyl 5-(*tert*-butyldiphenylsilyl)oxy-4-pentenoate in high yield. This means that the double bond conjugated with the ester moiety migrates to a deconjugated position by a ruthenium catalyst. We planned to prepare an enol ether from α,*β*-unsaturated compounds having an ether moiety in a tether using ruthenium-catalyzed isomerization of the double bond. As a result, silyl or benzyl enol ether was obtained from the α,*β*-unsaturated ester having alcohol protected by the silyl or benzyl group in a tether in high yield. In this reaction, double bond migration of α,*β*-unsaturated ketone and α,*β*-unsaturated amide took place to produce deconjugated compounds. Moreover, the double bond of α,*β*-unsaturated ester having a triple or double bond in a molecule migrated to produce conjugated enyne and diene. On the other hand, treatment of a bis-metalated compound having an α,*β*-unsaturated ester moiety or the double bond in a tether with $RuClH(CO)(PPh_3)_3$ gave allyl bis-metalated compound in good yield. These compounds are useful units in synthetic organic chemistry.

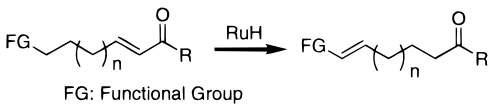
It is known that the isomerization reaction proceeds by acid, base, or organometallic complexes, and in general, a thermodynamically stable product is produced. Certain transition metal complexes, such as Fe, Pd, Rh, Pt, Ni, Ir, Ru, and Cr, are known as the catalysts for isomerization reaction.[1] $RuClH(CO)(PPh_3)_3$ is also known as a catalyst for isomerization, but the reaction usually affords a mixture of olefin isomers and it has rarely been used as an isomerization reagent in organic synthesis. However, several interesting examples have been shown in the literature.[2]

During the course of our study on ruthenium-catalyzed enyne cyclization,[3] we found that when a toluene solution of compound **2** was refluxed in the presence of 1.7 mol % of ruthenium catalyst **1** for 2 h, the double bond of α,*β*-unsaturated ester **2** was isomerized to provide deconjugated product **3** in high yield (Scheme 1).

Scheme 1



Scheme 2. Our Plan for Isomerization



Although α,*β*-unsaturated ester **2** is considered to be a thermodynamically stable compound compared with the deconjugated product **3**, in this case, the double bond conjugated with the ester part moved to nonconjugated part in the presence of ruthenium catalyst **1**. Presumably, the reaction would proceed through hydroruthenation and then *β*-hydrogen elimination. We were very interested in these results although the reason was not clear.

We planned to synthesize functionalized compounds from α,*β*-unsaturated carbonyl compounds using ruthenium catalyst as shown in Scheme 2. If an α,*β*-unsaturated carbonyl compound having a functional group at an appropriate position in a tether is treated with $RuClH(CO)(PPh_3)_3$, the double bond would move from the α,*β*-position of the carbonyl group to the position conjugated with the functional group.

Isomerization of the Double Bond of α,*β*-Unsaturated Carbonyl Compounds

When a toluene solution of **4a** was refluxed in the presence of **1** (5 mol %) for 2 h, silyl enol ether **5a** was obtained in 97% yield (ratio *E*/*Z*: 1:2.1, Scheme 3).

α,*β*-Unsaturated esters, **4b**−**4f**, having various carbon chains were treated in a similar manner, and the desired

(1) Fe: (a) Jolly, P. W.; Stone, F. G. A.; Mackenzie, K. *J. Chem. Soc.* **1965**, 6416. (b) Cowherd, F. G.; von Rosenberg, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 2157. (c) Hubert, A. J.; Georis, A.; Warin, R.; Teyssié, P. *J. Chem. Soc., Perkin Trans. 2* **1972**, 366. (d) Stille, J. K.; Becker, Y. *J. Org. Chem.* **1980**, *45*, 2139. Pd: (e) Golborn, P.; Scheinmann, F. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2870. Rh: (f) Corey, E. J.; Suggs, J. W. *J. Org. Chem.* **1973**, *38*, 3224. (g) Strohmeier, W.; Weigelt, L. *J. Organomet. Chem.* **1975**, *86*, C17. (h) Aresta, M.; De Fazio, M. *J. Organomet. Chem.* **1980**, *186*, 109. (i) Alper, H.; Hachem, K. *J. Org. Chem.* **1980**, *45*, 2269. (j) Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208. (k) Nemoto, H.; Jimenez, H. N.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 1304, and 1d. Ni: (l) Lochow, C. F.; Miller, R. G. *J. Org. Chem.* **1976**, *41*, 3020. Ir: (m) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1978**, 694. (n) Ohmura, T.; Shirai, Y.; Yamamoto, Y.; Miyaura, N. *Chem. Commun.* **1998**, 1337. Ru: (o) Suzuki, H.; Koyama, Y.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1979**, 1415. (p) Zoran, A.; Sasson, Y. *J. Org. Chem.* **1981**, *46*, 255. (q) Takahashi, M.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *Chem. Lett.* **1981**, 1435, and 1d. Cr: (r) Sodeoka, M.; Yamada, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1990**, *112*, 4906. (s) Yamada, H.; Sodeoka, M.; Shibasaki, M. *J. Org. Chem.* **1991**, *56*, 4569. Pt: (t) Clark, H. C.; Kurosawa, H. *Inorg. Chem.* **1973**, *12*, 357. (u) Clark, H. C.; Kurosawa, H. *Inorg. Chem.* **1973**, *12*, 1566.

(2) (a) Bingham, D.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1974**, 1519. (b) Matsuda, I.; Kato, T.; Sato, S.; Izumi, Y. *Tetrahedron Lett.* **1986** *27*, 5747. (c) Suzuki, H.; Yashima, H.; Hirose, T.; Takahashi, M.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1980** *21*, 4927. (d) Hirai, K.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1980**, *21*, 3413. (e) Hirai, K.; Suzuki, H.; Kashiwagi, H.; Moro-oka, Y.; Ikawa, T. *Chem. Lett.* **1982**, 23. (f) Hiraki, K.; Matsunaga, T. *Organometallics* **1994**, *13*, 1878.

(3) Nishida, M.; Adachi, N.; Onozuka, K.; Matsumura, H.; Mori, M. *J. Org. Chem.* **1998**, *63*, 9158.

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Scheme 3

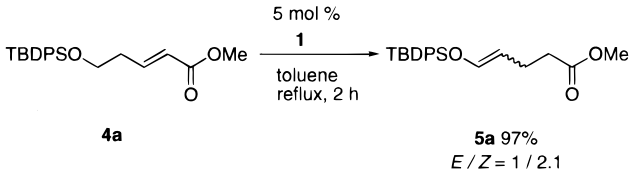
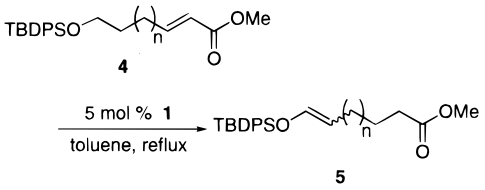


Table 1.[a]

run	substrate	*n*	time (h)	yield of **5** (%)	*E*/*Z*
1	**4b**	1	2	94	1/2.2
2	**4c**	2	2	80	1/2.2
3	**4d**	3	2	85	1/2.2
4	**4e**	4	4	78	1/2.0
5	**4f**	5	4	74	1/2.1

[a] The ratios are determined by ^{1}H NMR.

Scheme 4



silyl enol ethers **5b**−**5f** were obtained in good yields (Table 1). These results indicated that the double bond in α,*β*-unsaturated esters moved into a position conjugated with the silyl ether (Scheme 4).

Subsequently, isomerization of the double bond of α,*β*-unsaturated carbonyl compounds having various functional groups was carried out. From α,*β*-unsaturated ester **4g** having the benzyloxy group in a molecule, benzyl enol ether **5g** was obtained in high yield (Table 2, run 1). These results indicate that compounds having α,*β*-unsaturated ester and the hydroxyl group protected by the various groups in a molecule could be converted into compounds having saturated ester and the enol ether.

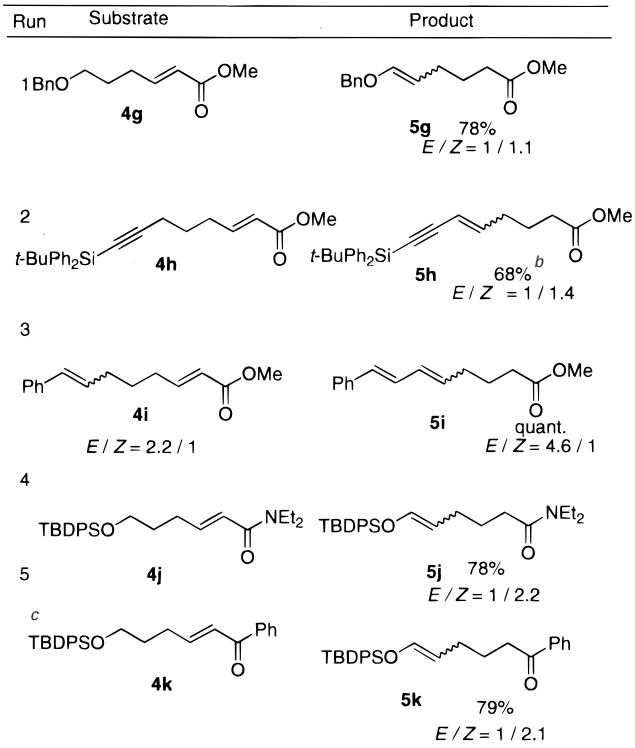
As the functional moiety, alkyne or alkene can be used, and 1,3-ynene **5h** and 1,3-diene **5i** were produced in good yields (runs 2 and 3). The isomerization of the double bond of α,*β*-unsaturated amide **4j** and ketone **4k** also proceeded smoothly to give saturated amide **5j** and ketone **5k** in 78% and 79% yields, respectively (runs 4 and 5). In the case of α,*β*-unsaturated ketone, the reaction time is longer than that of α,*β*-unsaturated ester or amide because of the strong coordination of the keto-carbonyl group to the ruthenium metal.

These results indicated that olefin isomerization of α,*β*-unsaturated carbonyl compounds proceeded smoothly using a catalytic amount of $RuClH(CO)(PPh_3)_3$ to give deconjugated carbonyl compounds in good yields and that α,*β*-unsaturated carbonyl compounds having the functional group in a tether could be converted into useful precursors for organic synthesis.

Synthesis of Allyl Bis-Metalated Compounds

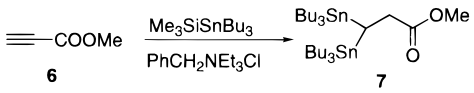
Subsequently, we tried to synthesize allyl bis-metalated compounds from bis-metalated compounds having an α,*β*-unsaturated ester part. We have already shown that the reaction of methyl propiolate **6** with $Me_3SiSnBu_3$ in the presence of $BnEt_3NCl$ gave methyl bis(tributylstannyl)propionate **7**, which is a useful C-3 unit for

Table 2. Isomerization of α,*β*-Unsaturated Ester[a]

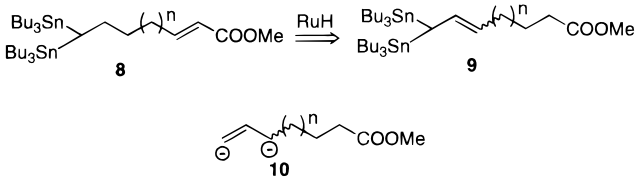


[a] All reactions were carried out in toluene upon refluxing for 2 h in the presence of $RuClH(CO)(PPh_3)_3$ (5 mol %). [b] Starting material was recovered in 23% yield. [c] The reaction time was 24 h.

Scheme 5. Synthesis of Bis-Stannylated Compound Having Olefin in a Tether



Scheme 6. Plan for Isomerization of Bis-Stannylated Compound



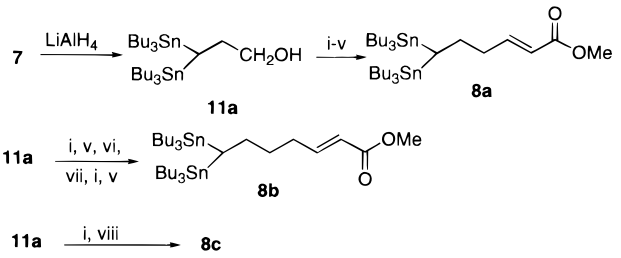
organic synthesis, in high yield.[4] If compound **8**, which would be synthesized from **7**, can be converted into the allyl bis-stannylated compound **9**, it would be used as an equivalent with 1,3-dianion **10** (Schemes 5 and 6). The synthesis of allyl bis-stannylated compounds is quite difficult, and there have only been a few reports on such synthesis.[5]

The starting bis-metalated compounds **8a** ($n = 0$) and **8b** ($n = 1$) having an α,*β*-unsaturated ester in a tether were synthesized from bis-stannylated compound **7** by the usual method, respectively (Scheme 7).

(4) (a) Mori, M.; Kaneta, N.; Isono, N.; Shibasaki, M. *Tetrahedron Lett.* **1991**, *32*, 6139. (b) Isono, N.; Mori, M. *Tetrahedron Lett.*, **1995**, *36*, 9345. (c) Isono, N.; Mori, M. *J. Org. Chem.* **1996**, *61*, 7867. (d) Isono, N.; Mori, M. *J. Org. Chem.* **1998**, *63*, 1773. (e) Wakamatsu, H.; Isono. N.; Mori, M. *J. Org. Chem.* **1997**, *62*, 8917.

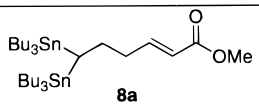
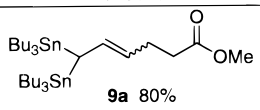
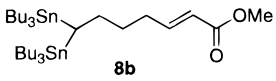
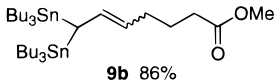
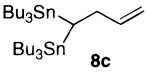
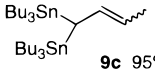
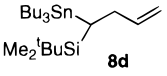
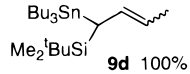
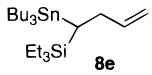
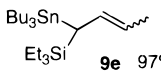
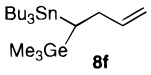
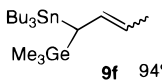
(5) (a) Reich, H. J.; Ringer, J. W. *J. Org. Chem.* **1988**, *53*, 455. (b) Lautens, M.; Huboux, A. H.; Chin, B.; Downer, J. *Tetrahedron Lett.* **1990**, *31*, 5829. (c) Madec, D.; Férézou, J.-P. *Tetrahedron Lett.* **1997**, *38*, 6657.

Scheme 7[a]



[a] Key: (i) $(COCl)_2$, DMSO; (ii) $Ph_3{}^+CH_2OCH_3Cl^-$, *t*-BuOK; (iii) concd HCl aq, MeOH; (iv) 2 N H_2SO_4; (v) $Ph_3P{=}CHCOOMe$; (vi) $NaBH_4$, cat. $NiCl_2$, MeOH; (vii) $LiAlH_4$, THF; (viii) Ph_3PCH_2.

Table 3. Synthesis of Allyl Bis-Metalated Compound[a]

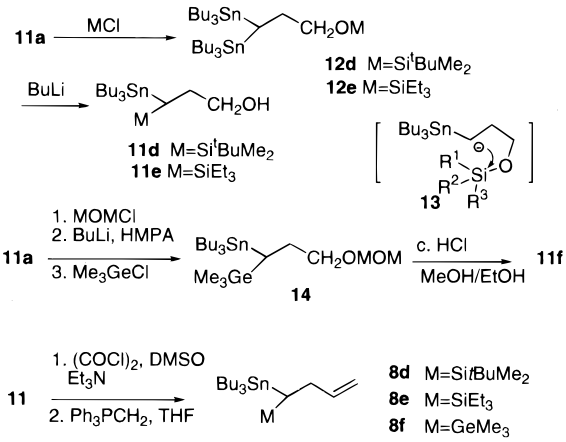
Run	Substrate	Product
1	 **8a**	 **9a** 80%
2	 **8b**	 **9b** 86%
3	 **8c**	 **9c** 95%
4	 **8d**	 **9d** 100%
5	 **8e**	 **9e** 97%
6	 **8f**	 **9f** 94%

[a] All reactions were carried out under reflux in toluene for 2−30 h in the presence of **1** (5 mol %). The ratio (*E*/*Z*) of **9** is 1/1.

When a toluene solution of **8a** was refluxed in the presence of a catalytic amount of **1** (5 mol %), allyl bis-stannylated compound **9a** was obtained in 80% yield (Table 3, run 1). In a similar manner, compound **8b** gave **9b** in 86% yield (run 2). Since we have been very interested in these allyl bis-stannylated compounds **9a** and **9b**, we examined to synthesize various allyl bis-metalated compounds from bis-metalated compounds **8c**−**f** having the olefin moiety in a tether. Bis-metalated compound **8c** was prepared from **11a** in a usual manner (Scheme 7), and **8d**−**f** were synthesized as follows (Scheme 8). Reaction of **11a** with *t*-$BuMe_2SiCl$ or Et_3SiCl gave silyl ether **12d** or **12e**, which was treated with BuLi to give silyl-stannylated compound **11d** or **11e** via **13**.[4d] Germylated compound **11f** was prepared from **11a**. Protection of the hydroxy group of **11a** with MOMCl followed by treatment with BuLi and then Me_3GeCl in the presence of HMPA gave **14**. Deprotection of the MOM group with concd HCl in MeOH afforded **11f**. Compounds **11d**−**f** were converted into **8d**−**f** in the usual manner.

The isomerization reaction of bis-metalated compounds **8c**−**f** also proceeded smoothly in the presence of **1** in toluene upon heating to give allyl bis-metalated compounds **9c**−**f** in high yields, respectively. (Table 3, runs 3−6). Thus, we could obtain various 1,1-bis-metalated

Scheme 8



compounds using $RuClH(CO)(PPh_3)_3$. Although these bis-metalated compounds are a mixture of *E*- and *Z*-isomers, it has been known that the reaction of a mixture of *E*- and *Z*-isomers of allylstannane with aldehyde gave a single coupling product.[6]

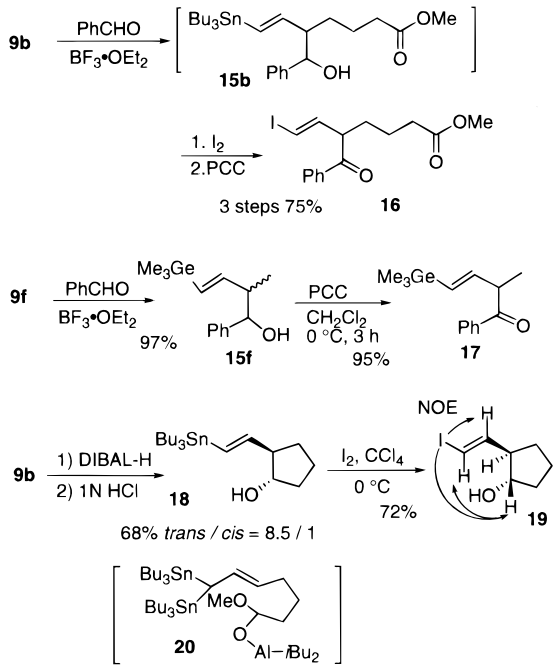
The Reactivity of Allyl Bis-Metalated Compound

To examine the reactivity of allyl bis-metalated compound **9**, the reaction of **9** with aldehyde was carried out. Compound **9b** was reacted with benzaldehyde in the presence of $BF_3{\cdot}Et_2O$ to give vinyl stannane. The crude product **15b** was treated with I_2 followed by PCC oxidation to give vinyl iodide **16** in good yield. Compound **9f** was treated with benzaldehyde in the presence of $BF_3{\cdot}Et_2O$ to give vinyl germanium compound **15f** in 97% yield, which was converted into ketone **17** having vinyl germanium moiety. Furthermore, intramolecular cyclization of **9b** was attempted. Treatment of **9b** with DIBAL-H followed by acid workup surprisingly gave the cyclized product **18** in one step. Probably, the reduction of **9b** with DIBAL-H gives **20** and the allyl stannyl moiety reacts with the acetal part of **20** to give **18**. To determine the stereochemistry of the cyclized product, compound **18** was treated with I_2 to give vinyl iodide **19**, whose NOE experiment indicated that *trans*-1,2-cyclopentanol was formed. These results indicate that allyl bis-metalated compound can react as an equivalent with 1,3-dianion **10**.

In summary, we found that olefin isomerization of α,β-unsaturated carbonyl compounds proceeded smoothly using a catalytic amount of $RuClH(CO)(PPh_3)_3$ to give deconjugated carbonyl compounds in good yields and that α,β-unsaturated ester having a functional group in a tether could be converted into a useful precursor for

(6) (a) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7107. (b) Yamamoto, Y.; Yatagai, H.; Ishihara, Y.; Maeda, N.; Maruyama, K. *Tetrahedron* **1984**, *40*, 2239. For another study of the stereochemistry in the reaction of allylstannane with aldehyde, see: (c) Marshall, J. A.; Welmaker, G. S. *J. Org. Chem.* **1992**, *57*, 7158. (d) Keck, G. E.; Abbott, D. E.; Boden, E. P.; Enholm, E. J. *Tetrahedron Lett.* **1984**, *25*, 3927. (e) Keck, G. E.; Abbott, D. E. *Tetrahedron Lett.* **1984**, *25*, 1883. (f) Gevorgyan, V.; Kadota, I.; Yamamoto, Y. *Tetrahedron Lett.* **1993**, *34*, 1313. (g) Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970. (h) Denmark, S. E.; Weber, E. J.; Wilson, T. M.; Willson, T. M. *Tetrahedron* **1989**, *45*, 1053. (i) Denmark, S. E.; Hosoi, S. *J. Org. Chem.* **1994**, *59*, 5133. (j) Keck, G. E.; Dougherty, S. M.; Savin, K. A. *J. Am. Chem. Soc.* **1995**, *117*, 6210. (k) Koreeda, M.; Tanaka, Y. *Chem Lett.* **1982**, 1297. (l) Koreeda, M.; Tanaka, Y. *Tetrahedron Lett.* **1987**, *28*, 143. (m) Hoffman, R. W. *Chem. Rev.* **1989**, *89*, 1841.

Scheme 9



organic synthesis. Moreover, allyl bis-metalated compounds could be synthesized from the corresponding bis-metalated compounds having the double bond in a tether.

Experimental Section

General Methods. Solvents were distilled under an argon atmosphere from sodium benzophenone (THF), CaH_2 (CH_2Cl_2, CCl_4), and $LiAlH_4$ (toluene). All other reagents were purified when necessary by standard procedures. All reactions were conducted under an argon atmosphere. ^1H NMR spectra were recorded at 500 MHz. ^{13}C NMR spectra were recorded at 125 MHz. ^1H NMR and ^{13}C NMR shifts (ppm) were reported relative to internal tetramethylsilane (Me_4Si). For ^{13}C NMR spectra, carbon type is defined as (CH_3), (CH_2), (CH), or (C) on basis of DEPT experiments. ^{119}Sn NMR spectra were recorded at 100 MHz. ^{119}Sn NMR shifts (ppm) were reported relative to external tetramethyltin (Me_4Sn).

General Procedure for Isomerization Reaction by a Ruthenium Catalyst. A toluene solution of **2**, **4**, or **8** (0.1 M) and $RuClH(CO)(PPh_3)_3$ (**1**) (5 mol %) was refluxed for 2−30 h. After the solvent was removed, the residue was purified by column chromatography on silica gel to provide **3**, **5**, or **9**.

Methyl 5-(*tert*-butyldiphenylsilyl)oxy-4-pentenoate (5a): IR (neat) 1740, 1660, 1428, 1114 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.06 (s, 0.32 × 9 H), 1.09 (s, 0.68 × 9 H), 2.15 (dt, J = 7.4, 7.5 Hz, 0.32 × 2 H), 2.27 (t, J = 7.4 Hz, 0.32 × 2 H), 2.44 (dd, J = 7.4, 7.6 Hz, 0.68 × 2 H), 2.57 (ddd, J = 6.9, 7.4, 7.6 Hz, 0.68 × 2 H), 3.59 (s, 0.32 × 3 H), 3.68 (s, 0.68 × 3 H), 4.49 (dt, J = 5.6, 6.9 Hz, 0.68 × 1 H), 5.08 (dt, J = 11.9, 7.5 Hz, 0.32 × 1 H), 6.20 (d, J = 5.6 Hz, 0.68 × 1 H), 6.30 (d, J = 11.9 Hz, 0.32 × 1 H), 7.36−7.67 (m, 10 H); MS m/z 368 (M^+), 353, 337, 311, 269, 213; HRMS m/z calcd for $C_{22}H_{28}O_3Si$ (M^+) 368.1808, found 368.1804.

Methyl 6,6-bis(tributylstannyl)-4-hexenoate (9a): IR (neat) 1744, 1464 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.75−0.91 (m, 30 H), 1.26−1.52 (m, 24 H), 1.78 (d, J = 12.2 Hz, 0.5 × 1 H, ^2J ($^{119}Sn-^1H$) = 27.2 Hz), 1.99 (d, J = 14.3 Hz, 0.5 × 1 H, ^2J ($^{119}Sn-^1H$) = 25.7 Hz), 2.16−2.34 (m, 4 H), 3.66 (s, 0.5 × 3 H), 3.67 (s, 0.5 × 3 H), 4.83−4.87 (m, 0.5 × 1 H), 5.02−5.08 (m, 0.5 × 1 H), 5.53−5.68 (m, 1 H); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ −4.3, −4.2; MS m/z 706 (M^+), 649 (M^+ − Bu), 417, 361, 291, 235, 179; HRMS m/z calcd for $C_{31}H_{64}O_2Sn_2$ (M^+) 708.2950, found 708.2953.

Methyl 5-((*E*)-2-Iodovinyl)-6-oxo-6-phenylhexanoate (16). To a solution of PhCHO (3 μL, 0.03 mmol) in CH_2Cl_2 was added BF_3·OEt_2 (4 μL, 0.03 mmol) at −78 °C, and the solution was stirred for 5 min. To this solution were added **9b** (21.1 mg, 0.03 mmol) and BF_3·OEt_2 (11.0 μL, 0.09 mmol). The resulting solution was stirred for 30 min at the same temperature. Saturated $NaHCO_3$ solution was added, and the aqueous phase was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude product was dissolved in CCl_4 and cooled to 0 °C. To this solution was added I_2 (excess) in CCl_4 until the reddish brown color was not consumed. The resulting solution was evaporated, and the residue was purified by column chromatography on silica gel (4:1−5:1 hexane/AcOEt) to provide a mixture of iodovinyl derivative. The product was dissolved in CH_2Cl_2 and cooled to 0 °C. To this solution were added MS4A (53.6 mg, powdered) and PCC (13.4 mg, 0.06 mmol). After the solution was stirred for 1 h at room temperature, Et_2O was added. The solution was passed through the Florisil tube and was evaporated. The residue was purified by column chromatography on silica gel (10:1 hexane/AcOEt) to provide a colorless oil of **16** (8.2 mg, 75%): IR (neat) 1736, 1682 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.59−1.72 (m, 3 H), 1.84−1.94 (m, 1 H), 2.33 (t, J = 7.1 Hz, 2 H), 3.65 (s, 3 H), 4.07−4.11 (m, 1 H), 6.30 (d, J = 14.6 Hz, 1 H), 6.63 (dd, J = 9.0, 14.6 Hz, 1 H), 7.48 (dd, J = 7.1, 7.4 Hz, 2 H), 7.59 (t, J = 7.4 Hz, 1 H), 7.93 (d, J = 7.1 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.5 (CH_2), 31.2 (CH_2), 33.7 (CH_2), 51.6 (CH_3), 53.3 (CH), 78.4 (CH), 128.4 (CH), 128.8 (CH), 133.5 (CH), 136.2 (C), 143.5 (CH), 173.5 (C), 198.5 (C); MS m/z 372 (M^+), 341, 245, 105, 77; HRMS m/z calcd for $C_{15}H_{17}O_3I$ (M^+) 372.0223, found 372.0220.

(*E*)-2-Methyl-4-(trimethylgermyl)-1-phenyl-3-buten-1-ol (15f). To a solution of PhCHO (10 μL, 0.10 mmol) in CH_2Cl_2 (0.9 mL) was added BF_3·OEt_2 (12 μL, 0.10 mmol) at −78 °C, and the solution was stirred for 5 min. To this solution was added **9f** (40.8 mg, 0.09 mmol) in CH_2Cl_2 (0.9 mL) and BF_3·OEt_2 (33 μL, 0.26 mmol). The resulting solution was stirred for 30 min at the same temperature. Saturated $NaHCO_3$ solution was added, and the aqueous phase was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (3:1:0.04 hexane/AcOEt/Et_3N) to provide a colorless oil of **15f** (23.9 mg, 97%): IR (neat) 3412, 1612, 1236 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.14 (s, 0.60 × 9 H), 0.21 (s, 0.40 × 9 H), 0.86 (d, J = 6.8 Hz, 0.40 × 3 H), 1.00 (d, J = 6.8 Hz, 0.60 × 3 H), 1.93 (d, J = 3.6 Hz, 0.60 × 1 H), 2.16 (d, J = 2.4 Hz, 0.40 × 1 H), 2.43−2.51 (m, 0.40 × 1 H), 2.55−2.60 (m, 0.60 × 1 H), 4.35 (dd, J = 2.4, 8.0 Hz, 0.40 × 1 H), 4.62 (dd, J = 3.6, 5.4 Hz, 0.60 × 1 H), 5.83−5.84 (m, 0.60 × 2 H), 5.88 (dd, J = 7.7, 18.3 Hz, 0.40 × 1 H), 6.00 (d, J = 18.3 Hz, 0.40 × 1 H), 7.24−7.33 (m, 5 H); MS m/z 265 (M^+ − Me + 1), 247, 225, 174, 159, 119, 107; HRMS m/z calcd for $C_{13}H_{19}OGe$ (M^+ − Me) 265.0648, found 265.0639.

(*E*)-2-Methyl-4-(trimethylgermyl)-1-phenyl-3-buten-1-one (17). To a solution of **15f** (7.5 mg, 0.03 mmol) in CH_2Cl_2 (1.0 mL) were added MS4A (46.4 mg, powdered) and PCC (11.6 mg, 0.05 mmol) at 0 °C, and the solution was stirred for 3 h at the same temperature. This reaction mixture was diluted with Et_2O, subjected to column chromatography on Florisil, and concentrated. The residue was purified by column chromatography on silica gel (1:1 hexane/benzene) to provide a colorless oil of **17** (7.0 mg, 95%): IR (neat) 1684, 1448, 1222 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 1.32 (d, J = 6.8 Hz, 3 H), 4.19 (dq, J = 6.7, 6.8 Hz, 1 H), 5.99 (d, J = 18.4 Hz, 1 H), 6.06 (dd, J = 6.7, 18.4 Hz, 1 H), 7.45 (dd, J = 7.5, 7.5 Hz, 2 H), 7.55 (dd, J = 7.5, 7.5 Hz, 1 H), 7.98 (d, J = 7.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −1.9 (CH_3), 17.2 (CH_3), 48.0 (CH), 128.5 (CH), 128.6 (CH), 132.8 (CH), 133.4 (CH), 136.6 (C), 143.3 (CH), 201.3 (C); MS m/z 277 (M^+), 263, 159, 119, 105, 77; HRMS m/z calcd for $C_{14}H_{20}OGe$ (M^+) 278.0726, found 278.0712.

***trans*-2-((*E*)-2-(Tributylstannyl)vinyl)-1-cyclopentanol (18).** To a solution of **9b** (44.3 mg, 0.06 mmol) in toluene

(1.0 mL) was added DIBAL-H in toluene solution (0.18 mL, 0.18 mmol, 1.01 M) at −78 °C. After the reaction mixture was stirred for 30 min at the same temperature, CH_3OH (0.1 mL) was added. The resulting solution was poured into 1 N HCl solution and extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (10:1 hexane/AcOEt) to provide a colorless oil of **18** (16.9 mg, 68%, trans/cis = 8.5/1): IR (neat) 3346 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.76−0.91 (m, 15 H), 1.27−1.77 (m, 16 H), 1.91−1.99 (m, 2 H), 2.36 (ddt, J = 7.1, 7.4, 7.9 Hz, 1 H), 3.61−3.66 (m, 0.11 × 1 H), 3.88−3.92 (m, 0.89 × 1 H), 5.87 (dd, J = 7.1, 18.9 Hz, 1 H), 5.98 (d, J = 18.9 Hz, 1 H); ^{119}Sn NMR (100 MHz, $CDCl_3$) δ −49.0; MS m/z 345 (M^+ − Bu + 1), 289, 233, 177; HRMS m/z calcd for $C_{15}H_{29}OSn$ (M^+ − Bu) 345.1240, found 345.1231.

***trans*-2-((*E*)-2-Iodovinyl)-1-cyclopentanol (19).** To a solution of **18** (19.5 mg, 0.05 mmol) in CCl_4 (2.0 mL) was added I_2 (excess) in CCl_4 solution at 0 °C until the reddish brown color was not consumed. The resulting solution was diluted with Et_2O, and 10% aqueous NH_4OH solution was added. The aqueous phase was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (10:1 hexane/AcOEt) to provide a colorless oil of **19** (8.3 mg, 72%): IR (neat) 3342, 1602 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.45 (ddd, J = 9.0, 12.9, 17.1 Hz, 1 H), 1.53−1.69 (m, 3 H), 1.72−1.80 (m, 1 H), 1.90−2.04 (m, 2 H), 2.37 (dddd, J = 8.0, 8.1, 8.2, 8.5 Hz, 1 H), 3.90−3.95 (m, 1 H), 6.12 (d, J = 14.3 Hz, 1 H), 6.47 (dd, J = 8.5, 14.3 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1 (CH_2), 29.1 (CH_2), 33.5 (CH_2), 55.1 (CH), 75.3 (CH), 77.6 (CH), 148.1 (CH); MS m/z 238 (M^+), 180, 167, 154, 127, 111, 93; HRMS m/z calcd for $C_7H_{11}OI$ (M^+) 237.9855, found 237.9869.

Supporting Information Available: ^1H NMR, ^{13}C NMR IR, and MASS spectral data of compounds **4e**,**f**, **4h**−**k**, **5b**−**k**, and **9b**−**f**. Experimental procedures for **8a**−**f**, **11e**, **12e**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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