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Isomerization of Olefins by Means of R_3SnH-Et_3B and Stereochemical Study on Reduction of Alkenyl Iodides

Masahiko Taniguchi, Kyoko Nozaki, Katsukiyo Miura,
Koichiro Oshima,* and Kiitiro Utimoto*
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606

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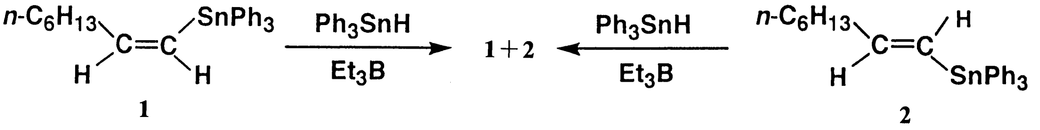
Isomerization of olefins with R_3SnH–Et_3B (R=Ph or *n*-Bu) system has been studied. Treatment of (*Z*)-1-triphenylstannyl-1-octene (**1**) or (*E*)-1-triphenylstannyl-1-octene (**2**) with a catalytic amount of Ph_3SnH–Et_3B provided an equilibrium mixture of **1**/**2**=2/8. Partial isomerization was observed in the reaction of trivial alkenes such as 6-dodecene and 2,2-dimethyl-3-dodecene with R_3SnH–Et_3B system. Whereas (*Z*)- or (*E*)-6-dodecene was recovered unchanged upon treatment with *n*-Bu_3SnH–Et_3B at −78 °C for 3 h, stirring a benzene solution of (*Z*)-6-dodecene, Ph_3SnH, and Et_3B at 60 °C for 5 h gave an isomeric mixture of (*Z*)-6-dodecene and (*E*)-6-dodecene (*Z*/*E*=64/36). Taking account of these results, the stereochemistry of the reduction of alkenyl iodides at −78 °C with R_3SnH–Et_3B system was studied. 6-Dodecenyl radical proved to isomerize much more rapidly than it abstracts a hydrogen from R_3SnH.

(1) Isomerization of Alkenylstannanes with R_3SnH–Et_3B System. We have reported that hydrostannation[1)] or hydrogermylation[2)] of acetylenes proceeded easily with Ph_3SnH–Et_3B or Ph_3GeH–Et_3B system to give alkenylstannanes or alkenylgermanes. Hydrogermylation of acetylenes with Ph_3GeH–Et_3B proved to be effective for the stereoselective formation of (*E*)- or (*Z*)-alkenylgermanes. Whereas Et_3B catalyzed addition of Ph_3GeH to 1-dodecyne at −78 °C afforded (*Z*)-1-triphenylgermyl-1-dodecene exclusively, the addition of Ph_3GeH at 60 °C provided (*E*)-1-triphenylgermyl-1-dodecene as a single product. In contrast, Et_3B-induced hydrostannation of 1-dodecyne with Ph_3SnH gave a 3/7—2/8 mixture of (*Z*)- and (*E*)-1-triphenylstannyl-1-dodecene irrespective of the reaction conditions (long reaction times, excess Ph_3SnH, and different reaction temperature (−78 °C∼100 °C). In order to find the reason for the different stereochemical outcome between hydrostannation and hydrogermylation, we studied the isomerization of alkenylstannanes with R_3SnH–Et_3B system and found that treatment of (*E*)- or (*Z*)-alkenylstannanes with a catalytic amount of *n*-Bu_3SnH–Et_3B or Ph_3SnH–Et_3B gave the same ratio of (*E*)- and (*Z*)-alkenylstannanes.

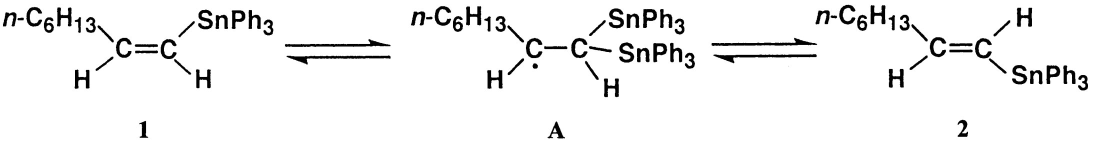
Treatment of a benzene solution of (*Z*)-1-triphenylstannyl-1-octene **1** with a catalytic amount of Ph_3SnH and Et_3B (0.2 mmol each) at 25 °C for 12 h gave a mixture of (*E*)-1-triphenylstannyl-1-octene **2** and (*Z*)-isomer **1** (**1**/**2**=2/8). (*E*)-Isomer **2** also provided the same mixture (**1**/**2**=2/8) upon treatment with Ph_3SnH–Et_3B (Scheme 1).

The isomerization is explained by addition-elimination sequences of triphenylstannyl radical as in the case of the isomerization of alkenylgermane.[2)] The stannyl radical, $Ph_3Sn\cdot$ attacks the olefinic carbon bearing stannyl groups to give a radical intermediate **A**. Free rotation around C–C single bond followed by elimination of triphenylstannyl radical would induce the stereochemical scrambling of the olefin and the composition of the stereoisomeric mixture reaches the thermodynamic equilibrium (*Z*/*E*=2/8, Scheme 2). This mechanism[3)] is supported by the following experiments.

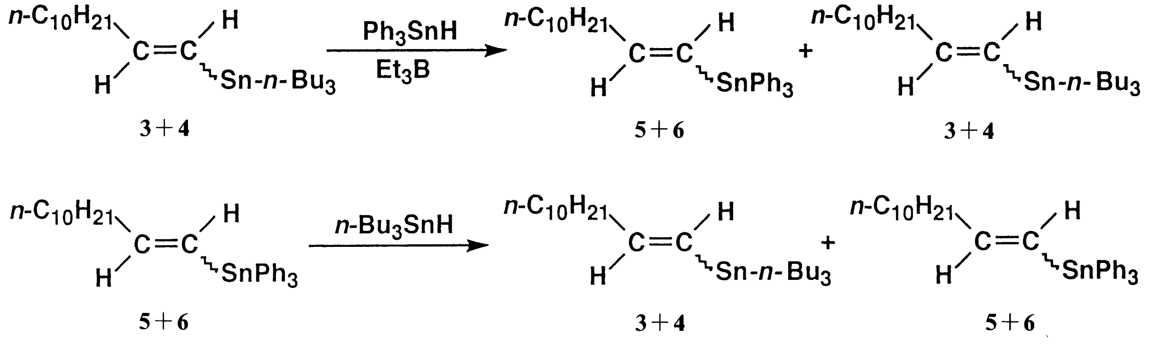
Treatment of 1-tributylstannyl-1-dodecene (a mixture of (*Z*)-isomer **3** and (*E*)-isomer **4**, **3**/**4**=3/7, 1.0 mmol) with Ph_3SnH–Et_3B (1.0–0.2 mmol) at 25 °C for 12 h gave a mixture of (*Z*)-1-triphenylstannyl-1-dodecene **5**, (*E*)-isomer **6** (**5**/**6**=2/8), and 1-tributylstannyl-1-dodecene (**3**/**4**=3/7, **3**+**4**/**5**+**6**=2/3). Moreover, treatment of 1-triphenylstannyl-1-dodecene (**5**/**6**=2/8) with *n*-Bu_3SnH–Et_3B (1.0–0.2 mmol) gave the same mixture



Scheme 1.



Scheme 2.



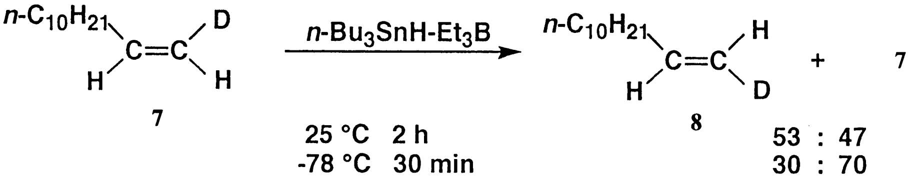
Scheme 3.

of **3**, **4**, **5**, and **6** (**3**+**4**/**5**+**6**=2/3) (Scheme 3).

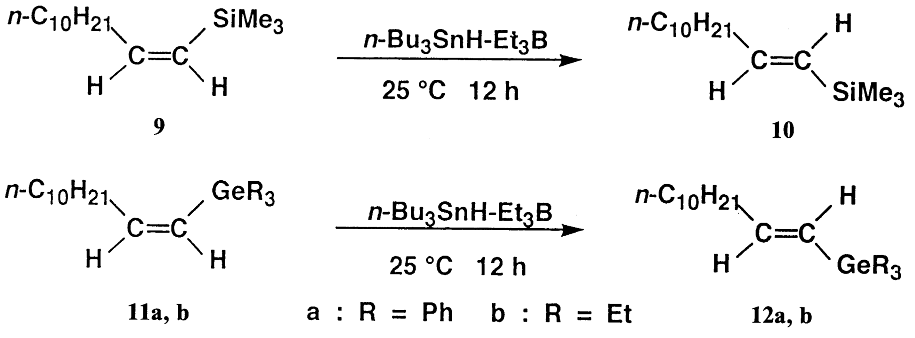
These facts might yield a following conclusion of the stereochemical outcome of hydrostannation. As in the case of hydrogermylation, hydrostannation of 1-alkyne provides (*Z*)-1-triphenylstannyl-1-alkene as a primary product. Then, the (*Z*)-1-triphenylstannyl-1-alkene isomerizes to thermodynamic equilibrium mixture of (*E*) and (*Z*) isomer even at −78 °C by the action of a Ph_3Sn radical. The different stereochemical outcome between hydrostannation and hydrogermylation might be attributed to two factors: (1) small energy difference between (*E*)-1-alkenylstannanes and (*Z*)-1-alkenylstannanes compared with that between (*E*)-1-alkenylgermanes and (*Z*)-1-alkenylgermanes and (2) a facile isomerization of primary hydrostannation products compared with hydrogermylation products under the reaction conditions. Whereas the attack of Ph_3Sn radical on 1-stannyl-1-alkene is fast even at −78 °C, the attack of Ph_3Ge radical on 1-germyl-1-alkene is sluggish at low temperature and requires heating at 60 °C to complete the isomerization.

(2) Isomerization of Other Alkenes with R_3SnH-Et_3B System. Here we describe the isomerization of other various kinds of alkenes with R_3SnH–Et_3B system. Stirring a benzene solution of (*Z*)-1-deuterio-1-dodecene **7** (1.0 mmol) in the presence of *n*-Bu_3SnH (0.2 mmol) and Et_3B (0.2 mmol) at 25 °C for 2 h gave an equilibrium mixture of (*Z*) and (*E*) isomer **8** (**7**/**8**=47/53). A mixture of **7**/**8**=70/30 was obtained after treatment of **7** with *n*-Bu_3SnH–Et_3B at −78 °C for 30 min (Scheme 4).

The isomerization of (*Z*)-1-trimethylsilyl-1-dodecene **9** and (*E*)-1-trimethylsilyl-1-dodecene **10** was examined. Treatment of a toluene solution of (*Z*)-1-trimethylsilyl-1-dodecene **9** with *n*-Bu_3SnH–Et_3B at −78 °C for 30 min provided a 1/1 mixture of **9** and **10**. Stirring at 25 °C for 12 h gave (*E*) isomer **10** exclusively. On the other hand, (*E*)-isomer **10** was recovered unchanged after treatment with Ph_3SnH–Et_3B or *n*-Bu_3SnH–Et_3B at 25 °C for 12 h. In a similar fashion, (*Z*)-1-triphenylgermyl-1-dodecene **11a** or (*Z*)-1-triethylgermyl-1-dodecene **11b** afforded the respective (*E*)-1-triphenylgermyl-1-dodecene **12a** or (*E*)-1-triethylgermyl-1-dodecene



Scheme 4.



Scheme 5.

12b with high stereoselectivity (E/Z=>20/<1) upon treatment with Ph_3SnH–Et_3B (0.1 mmol each) at 25 °C for 12 h (Scheme 5).

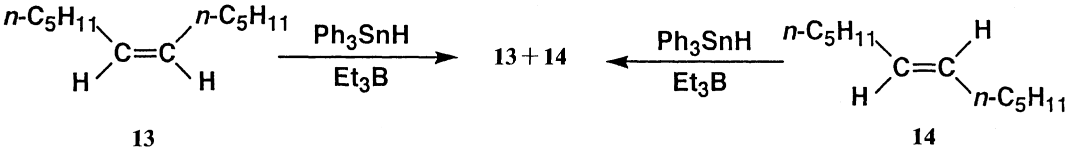
(*Z*)-6-Dodecene or (*E*)-6-dodecene was recovered unchanged after treatment with *n*-Bu_3SnH–Et_3B at −78 °C for 3 h. However, partial isomerization was observed in the reaction at 25 °C. Treatment of (*Z*)-6-dodecene with Ph_3SnH–Et_3B (0.2 mmol each) or *n*-Bu_3SnH–Et_3B (0.2 mmol each) at 25 °C for 12 h gave a mixture of Z/E=63/37 or 73/27. A similar isomeric ratio (Z/E=64/36) was obtained after heating at 60 °C for 5 h. Partial isomerization was also observed in the reaction of (*E*)-6-dodecene with Ph_3SnH–Et_3B (0.2 mmol each). Stirring a benzene solution of (*E*)-6-dodecene, Ph_3SnH, and Et_3B at 60 °C for 6 h gave an isomeric mixture of (*E*)- and (*Z*)-6-dodecene (E/Z=93/7). Complete isomerization to the equilibrium mixture (E:Z=85:15[4)]) did not occur in either direction (Scheme 6).

Heating a benzene solution of (*Z*)-2,2-dimethyl-3-dodecene at 60 °C for 5 h in the presence of a catalytic amount of Ph_3SnH–Et_3B (0.2 mmol each) gave a mixture of (*E*)-2,2-dimethyl-3-dodecene and *Z*-isomer (E/Z=20/80, Scheme 7). This result shows a sharp contrast to the Ph_3GeH–Et_3B system[2)] which gave the completely isomerized product (E/Z=>20/<1). Thus, Ph_3SnH–Et_3B system proved to be as effective as Ph_3GeH–Et_3B system for the isomerization of (*Z*)-1-deuterio-1-dodecene, 1-trimethylsilyl-1-dodecene, and 1-trialkylgermyl-1-dodecene, but not as effective as Ph_3GeH–Et_3B for the isomerization of 6-dodecene and 2,2-dimethyl-3-dodecene.

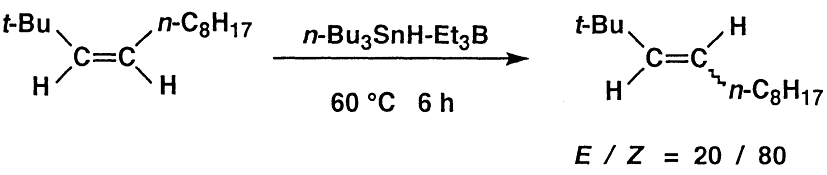
Triphenylgermane easily added to terminal olefins. For instance, Et_3B catalyzed hydrogermylation of 1-dodecene with Ph_3GeH provided dodecyltriphenylgermane in 89% yield.[2)] However, an addition product such as $RCH(SnPh_3)CH_2R$ or $RCH_2CH_2SnPh_3$ was not observed in the reaction of RCH=CHR or $RCH=CH_2$ with Ph_3SnH.[5)]

(3) Stereochemical Study on the Reduction of Alkenyl Iodide with *n*-Bu_3SnH–Et_3B System. A characteristic of Et_3B induced reaction is that the triphenylstannyl radical or tributylstannyl radical can be generated at low temperature such as −78 °C and thereby the hydrostannation of acetylenes or reduction of organic halides proceeds at such low temperature. Based on the experiments that have been described in section (1) and (2), the stereochemistry of the reduction of alkenyl iodides with a Ph_3SnH–Et_3B system at −78 °C has been studied. Treatment of (*Z*)-1-deuterio-1-iodo-1-dodecene or (*E*)-1-deuterio-1-iodo-1-dodecene with *n*-Bu_3SnH–Et_3B at −78 °C resulted in formation of similar isomeric mixtures of (*E*)- and (*Z*)-1-deuterio-1-dodecene (E/Z=61/39—63/37).[6)] In these experiments, primary product, 1-deuterio-1-dodecene generated by the reduction with *n*-Bu_3SnH–Et_3B isomerized under the reaction conditions as mentioned above. Thus, the stereochemical outcome of the final products does not reflect the stereochemical results of the reduction. (*E*)-1-Iodo-1-triethylsilyl-1-dodecene gave a mixture of (*Z*)-1-triethylsilyl-1-dodecene and (*E*)-isomer (E/Z=56/44) upon treatment with *n*-Bu_3SnH–Et_3B at −78 °C. Meantime, (*Z*)-1-iodo-1-triethylsilyl-1-dodecene afforded a similar mixture of Z/E=57/43. These results might indicate that 1-triethylsilyl-1-alkenyl radical isomerizes much more rapidly than it abstracts a hydrogen atom from tributyltin hydride. However, tin radical could also induce partial isomerization of the product, (*Z*)-1-triethylsilyl-1-dodecene even at −78 °C as stated in section (2) and this makes the reaction mechanism more complicated.

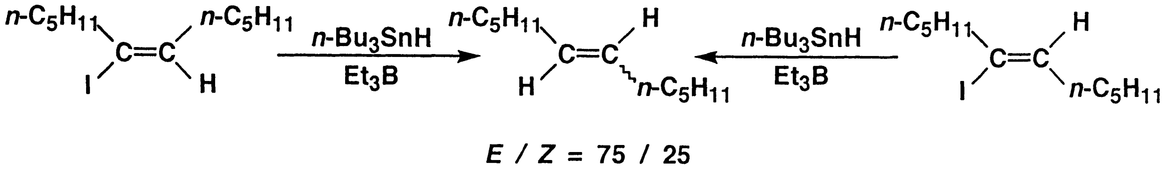
The stereochemistry of alkenyl radical may be discussed more clearly in the reduction of (*E*)-6-iodo-6-dodecene and (*Z*)-6-iodo-6-dodecene because a primary reduction product, (*E*)-6-dodecene or (*Z*)-6-dodecene does not isomerize at −78 °C with R_3SnH–Et_3B system. Treatment of (*E*)-6-iodo-6-dodecene or (*Z*)-6-iodo-6-dodecene with *n*-Bu_3SnH–Et_3B at −78 °C for 30 min provided a same isomeric mixure of (*E*)-6-dodecene and (*Z*)-6-dodecene (E/Z=75/25) (Scheme 8).[7)] The results have been explained by fast equilibration of two configurations of the alkenyl radical before hydrogen transfer



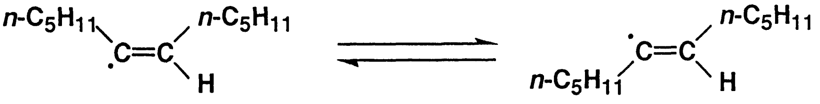
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

(Scheme 9).

Experimental

Preparation of Alkenylstannanes. (*E*)-1-Triphenylstannyl-1-octene (**2**) and (*E*)-1-triphenylstannyl-1-dodecene were prepared according to the reported procedure.[8)]

(Z)-1-Triphenylstannyl-1-octene (1). Butyllithium (1.6 M hexane solution, 1 M=1 mol dm^{-3} 1.34 ml, 2.2 mmol) was added to a solution of (*Z*)-1-iodo-1-octene (0.48 g, 2.0 mmol) in THF (10 ml) at −78 °C under argon atmosphere. After stirring at −78 °C for 30 min, Ph_3SnCl (0.80 g, 2.1 mmol) was added and the resulting mixture was stirred at −78 °C for 30 min, then 25 °C for 1 h. The mixture was poured into a saturated aqueous NH_4Cl solution and extracted with ethyl acetate three times. Combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to obtain a title compound (0.18 g, 20% yield) which was contaminated by (*E*)-isomer **2** (*Z*/*E*=9/1).

Isomerization of 1-Triphenylstannyl-1-octene. A hexane solution (5.0 ml) of (*Z*)-1-triphenylstannyl-1-octene (**1**, 0.23 g, 0.5 mmol) was stirred at 25 °C for 12 h in the presence of Ph_3SnH (35 mg, 0.1 mmol) and Et_3B (1.0 M hexane solution, 0.1 ml, 0.1 mmol). Examination of ^1H NMR of crude product revealed that the product consists of (*Z*)- and (*E*)-1-triphenylstannyl-1-octene (**1**/**2**=2/8). The same isomeric mixture was obtained starting from (*E*)-1-triphenylstannyl-1-octene (**2**) upon treatment with a catalytic amount of Ph_3SnH–Et_3B at 25 °C for 10 h.

Reaction of 1-Tributylstannyl-1-dodecene with Triphenyltin Hydride in the Presence of Et_3B. Triethylborane (1.0 M hexane solution, 0.07 ml, 0.07 mmol) was added to a benzene (2 ml) solution of 1-tributylstannyl-1-dodecene (a mixture of (*Z*)-isomer **3** and (*E*)-isomer **4**, **3**/**4**=3/7, 152 mg, 0.33 mmol, prepared by hydrostannation of 1-dodecyne with *n*-Bu_3SnH at 80 °C in benzene[9)]) and triphenyltin hydride (117 mg, 0.33 mmol). The mixture was stirred for 12 h at 25 °C. Concentration of the resulting mixture gave an oil which was purified by alumina column chromatography using hexane as an eluant to give 1-tributylstannyl-1-dodecene (62 mg, 42% yield, **3**/**4**=3/7) along with 1-triphenylstannyl-1-dodecene (110 mg, 64% yield, **5**/**6**=2/8). Reaction of 1-triphenylstannyl-1-dodecene (**5**/**6**=2/8, prepared by Et_3B induced hydrostannation of 1-dodecyne[1)]) with *n*-Bu_3SnH–Et_3B also provided the same mixture of **3**, **4**, **5**, and **6**.

Preparation of Alkenes. (*Z*)-1-Deuterio-1-dodecene (**7**), (*Z*)-1-trimethylsilyl-1-dodecene (**9**), (*Z*)-1-triphenylgermyl-1-dodecene (**11a**), (*Z*)-1-triethylgermyl-1-dodecene (**11b**), and (*Z*)-2,2-dimethyl-3-dodecene were prepared by hydroalumination of the corresponding acetylenic compounds. (*Z*)-6-Dodecene and (*E*)-6-dodecene were purchased from Farchan Laboratories, Inc. and used without further purification. (*E*)-6-Iodo-6-dodecene was prepared by hydroalumination followed by treatment with iodine. (*Z*)-6-Iodo-6-dodecene was prepared from 6-dodecyne by treatment with hydroiodic acid according to the reported procedure.[10)]

General Procedure for the Isomerization of Alkenes. The reaction of (*Z*)-1-trimethylsilyl-1-dodecene (**9**) with *n*-Bu_3SnH–Et_3B is representative. Triethylborane (1.0 M, 0.1 ml, 0.1 mmol) was added to a benzene (5.0 ml) solution of **9** (0.24 g, 1.0 mmol) and *n*-Bu_3SnH (60 mg, 0.2 mmol) at 25 °C under argon atmosphere. The resulting mixture was stirred for 12 h at 25 °C. Iodoethane (0.60 g, 0.4 mmol) was added to destroy excess *n*-Bu_3SnH and the whole was stirred for another 30 min at 25 °C. The reaction mixture was concentrated in vacuo and the residual oil was submitted to silica-gel column chromatography to give (*E*)-1-trimethylsilyl-1-dodecene (**10**, 0.20 g) in 85% yield. The reaction at −78 °C was performed in similar fashion. Triethylborane was added to a toluene solution of **9** and *n*-Bu_3SnH at −78 °C. After stirring for 30 min at −78 °C, EtI was added at the same temperature. The resulting mixture was stirred at −78 °C for another 30 min. Extractive workup followed by purification by silica-gel column chromatography gave 1-trimethylsilyl-1-dodecene as a mixture of (*Z*)-isomer **9** and (*E*)-isomer **10** (**9**/**10**=1/1) in 88% yield.

General Procedure for the Reduction of Alkenyl Iodides. The hydrodehalogenation of (*E*)-6-iodo-6-dodecene is representative. A solution of *n*-Bu_3SnH (0.33 g, 1.1 mmol) in toluene (1.0 ml) and Et_3B (1.0M hexane solution, 0.1 ml, 0.1 mmol) were added successively to a solution of (*E*)-6-iodo-6-dodecene (0.29 g, 1.0 mmol) in toluene (5.0 ml) at −78 °C and the resulting mixture was stirred at −78 °C for 30 min. EtI (0.31 g, 0.2 mmol) was added and the whole was stirred for another 30 min. The mixture was transferred into 100 ml round-bottomed flask using 25 ml of methanol. The solvent was evaporated as an azeotropic mixture to afford a crude oil which was submitted to silica-gel column chromatography to give 6-dodecene (0.15 g, *Z*/*E*=25/75) in 90% yield.

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