Pergamon

*Tetrahedron* Vol. 51, No. 43, pp. 11681-11692, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4020/95 $9.50+0.00

0040-4020(95)00700-2

# A Facile Preparation of Alkenyl- and Allenylmetallic Compounds by Means of Iodine-Metal Exchange and Their Use in Organic Synthesis

**Hiroshi Shinokubo, Hiroaki Miki, Toshiaki Yokoo, Koichiro Oshima,* and Kiitiro Utimoto***

Division of Material Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

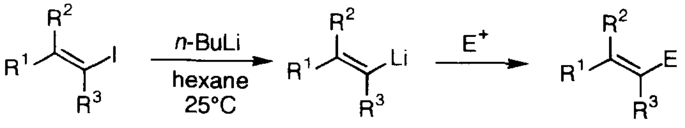
**Abstract:** Stereospecific lithium-halogen exchange of alkenyl iodides was performed upon treatment with butyllithium in non-polar solvents such as hexane, benzene, and toluene at 25 °C to provide alkenyllithiums quantitatively with retention of the configuration. Metal-iodine exchange of allenyl iodides with *n*-BuLi, *i*-PrMgBr or $Et_2Zn$ was also performed effectively to afford the corresponding allenylmetallic reagents. An addition of carbonyl compounds to the metallic reagents gave homopropargylic alcohols with high regioselectivity in good yields.

## *(1) A room temperature preparation of alkenyllithiums by lithium-halogen exchange between alkenyl iodides and n-BuLi in hydrocarbon solvents*

Numerous methods for the preparation of organometallic compounds are known. Among them, the metal-halogen exchange reaction is extremely valuable for preparing organolithium compounds and particularly useful for preparing alkenyllithium compounds by reaction of alkyllithium with alkenyl halides.[1] Alkenyllithiums are generally prepared by an addition of *tert*-butyllithium to 1-bromo-1-alkenes or 1-iodo-1-alkenes at low temperature such as −78 °C or −120 °C.[2] The reactions are normally carried out in ether or tetrahydrofuran (THF). One feature of the exchange reaction that can cause complications is the presence of the alkyl halide product. When the desired organolithium reagent is warmed for subsequent reaction, it can couple with the alkyl halide, giving alkenyl-alkyl. This type of side reaction may be avoided by the use of two equivalents of *tert*-butyllithium. The second equivalent rapidly reacts with the *tert*-butyl halide formed to give the innocuous by-products lithium halide and isobutene. Here we want to report[3] that the side reaction can be eliminated by an appropriate selection of the reaction conditions and treatment of alkenyl iodides with butyllithium at room temperature in hydrocarbons resulted in a quantitative formation of alkenyllithiums which react with various electrophiles to afford the corresponding adducts in good yields.[4]

Butyllithium (1.5 mmol) was added to a hexane solution of (*E*)-1-iodo-1-dodecene (1.0 mmol) at 25 °C and the resulting solution was stirred at 25 °C for 15 min. An addition of pentanal (1.2 mmol) afforded the corresponding allylic alcohol, (*E*)-6-heptadecen-5-ol quantitatively. One and a half molar equivalent of butyllithium was used for the exchange reaction to obtain alkenyllithium quantitatively. The use of 1.2 molar equivalent or 1.0 molar equivalent of butyllithium decreased the yield of the adduct, (*E*)-6-heptadecen-5-ol to 78% or 72%, respectively. The other results are summarized in Table 1.

Table 1. Preparation of alkenyllithiums and their reaction with electrophiles[a]



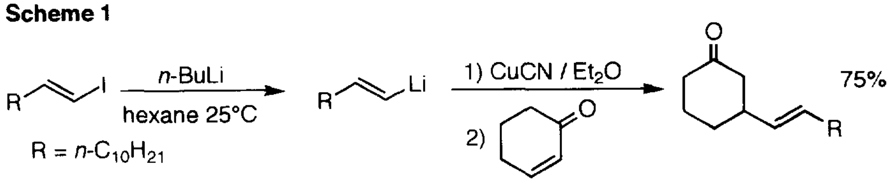
| Run | Alkenyl Iodide $R^1$ | $R^2$ | $R^3$ | Electrophile | Yield of Adduct (%) |
|---|---|---|---|---|---|
| 1 | H | H | H | PhCHO | 55 |
| 2 | H | H | H | *c*-$C_6H_{11}$CHO | 61 |
| 3 | *n*-$C_{10}H_{21}$ | H | H | $D_2O$ | 96 |
| 4 | *n*-$C_{10}H_{21}$ | H | H | PhCHO | 80 |
| 5 | *n*-$C_{10}H_{21}$ | H | H | *c*-$C_6H_{11}$CHO | 100 |
| 6 | *n*-$C_{10}H_{21}$ | H | H | cyclohexanone | 100 |
| 7 | *n*-$C_{10}H_{21}$ | H | H | $PhCOCH_3$ | 87 |
| 8 | *n*-$C_{10}H_{21}$ | H | H | $Me_3SiCl$[b] | 95 |
| 9 | *n*-$C_{10}H_{21}$ | H | H | $CH_3I$[c] | 85 |
| 10 | H | *n*-$C_{10}H_{21}$ | H | *n*-$C_4H_9$CHO | 100 |
| 11 | H | *n*-$C_{10}H_{21}$ | H | *c*-$C_6H_{11}$CHO | 87 |
| 12 | H | *n*-$C_{10}H_{21}$ | H | $CH_3COCH_3$ | 62 |
| 13 | H | *n*-$C_{10}H_{21}$ | H | cyclohexanone | 77 |
| 14 | H | *n*-$C_{10}H_{21}$ | H | $Me_3SiCl$[b] | 91 |
| 15 | *n*-$C_5H_{11}$ | H | *n*-$C_5H_{11}$ | *n*-$C_4H_9$CHO | 90 |
| 16 | *n*-$C_5H_{11}$ | H | *n*-$C_5H_{11}$ | $PhCOCH_3$ | 67 |
| 17 | *n*-$C_5H_{11}$ | H | *n*-$C_5H_{11}$ | $Me_3SiCl$[b] | 100 |
| 18 | *n*-$C_5H_{11}$ | H | *n*-$C_5H_{11}$ | $CH_3I$[c] | 100 |
| 19 | H | H | $CH_2OH$[d] | PhCHO | 50 |

a) Iodoalkene (1.0 mmol), butyllithium (1.5 mmol), and carbonyl compound (1.2 mmol) were employed. b) A solution of $Me_3SiCl$ (1.2 mmol) in THF (1.0 ml) was added to alkenyllithiums. c) $CH_3I$ (1.0 ml) was added to alkenyllithiums. d) Three molar equivalents of butyllithium were used.

Several features of the reaction are worth noting. (1) Conversion of alkenyl bromide to alkenyllithium was not so effective as alkenyl iodide. For instance, treatment of (*E*)-1-bromo-1-dodecene with butyllithium at 25 °C followed by an addition of pentanal to the resulting 1-dodecenyllithium gave (*E*)-6-heptadecen-5-ol in only 40% yield.[5] (2) A choice of solvent is critical for the successful reaction. Hexane and benzene proved to be equally effective solvents for the metal-halogen exchange reaction. Treatment of (*Z*)-1-iodo-1-dodecene with butyllithium in hexane or benzene and successively with pentanal provided (*Z*)-6-heptadecen-5-ol quantitatively. In other solvents such as toluene, ether, and THF, (*Z*)-6-heptadecen-5-ol was obtained in 85%, 58%, and <5% yields, respectively. In the case of the reactions in ether and THF, starting 1-iodo-1-dodecene was consumed completely and unidentified complex mixture was obtained in addition to (*Z*)-6-heptadecen-5-ol. (3) Alkenyllithiums were stable in hydrocarbon solvents and potential side-reactions such as alkylation of, or elimination from the organic halide (iodobutane), which was produced in the metal-halogen exchange process, were not troublesome. Thus, butylated alkene could not be observed in the reaction mixture.[6] (4) Stereochemistry of alkenyl iodides was completely conserved during the reaction. Whereas (*E*)-1-iodo-1-dodecene gave (*E*)-6-heptadecen-5-ol exclusively upon treatment with butyllithium and subsequent addition of pentanal, (*Z*)-1-iodo-1-dodecene afforded the corresponding (*Z*)-isomer selectively (Run 10). (5) Dialkyl substituted iodoalkene ((*E*)-6-iodo-6-dodecene, Run 15–18) provided the corresponding alkenyllithium effectively upon treatment with butyllithium as well as monoalkyl substituted iodoalkenes or iodoethene (Run 1 and 2). (6) An addition of three molar equivalents of butyllithium to 2-iodo-2-propen-1-ol gave alkenyllithium which afforded the corresponding allylic diol in moderate yield upon treatment with benzaldehyde (Run 19).

Alkenyllithiums were easily transformed into organometallics such as cuprates. For instance, an addition of CuCN[7] to a solution of alkenyllithium, prepared from (*E*)-1-iodo-1-dodecene and butyllithium, provided alkenylcuprate which reacted with 2-cyclohexenone to give 1,4-adduct in 75% yield (Scheme 1).

**Scheme 1**



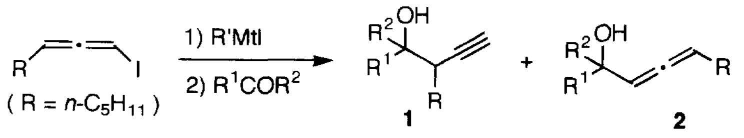
*(2) Preparation of allenylmetallics by metal-iodine exchange between allenyl iodides and n-BuLi, i-PrMgBr, or $Et_2$ Zn*

The chemistry of acetylene and allene has attracted much attention during the past two decades.[8] One of the most versatile preparative methods for these compounds is a use of propargyl and allenyl organometallics. Organometallics of allenic structure are usually prepared by the reactions of metals with propargylic or allenic halides, or by metalation with alkyllithiums of the corresponding hydrocarbons.[9] Here we wish to report a facile alternative approach to allenic organometallics based on the exchange reaction between allenyl iodides and organometallics such as *n*-BuLi, *i*-PrMgBr or $Et_2Zn$.

The preparative method for alkenyllithiums described in section (1) was applied to the generation of allenyl organometallic reagents. An addition of *n*-BuLi to a hexane or toluene solution of 1-iodo-1,2-octadiene at –78 °C gave the corresponding organolithium compound which provided the adducts upon treatment with carbonyl compounds such as PhCHO and $PhCOCH_3$.[10,11] Not only butyllithium but also *i*-

PrMgBr and $Et_2Zn$ were also effective for the preparation of organometallic reagents from 1-iodo-1,2-alkadienes via metal-halogen exchange. The results are summarized in Table 2.

Table 2. Preparation of allenylmetallic reagents and their reaction with carbonyl compounds



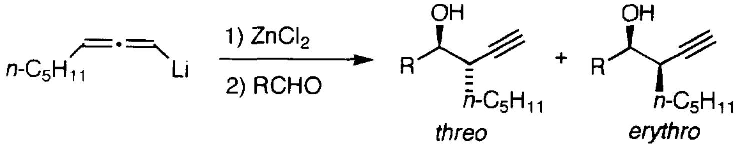
| R'Mtl | Solvent | $R^1COR^2$ | Yield | Ratio of **1**:**2** | *erythro*/*threo* of **1** |
|---|---|---|---|---|---|
| *n*-BuLi | hexane | PhCHO | 83% | >99 : <1 | 55 / 45 |
| *n*-BuLi | toluene | *n*-$C_4H_9CHO$ | 87% | >99 : <1 | 31 / 69 |
| *n*-BuLi | toluene | *t*-BuCHO | 64% | >99 : <1 | <1 / >99 |
| *n*-BuLi | toluene | $PhCOCH_3$ | 96% | 92 : 8 | 40 / 60 |
| *n*-BuLi | toluene | *n*-$C_9H_{19}COCH_3$ | 83% | 50 : 50 | 50 / 50 |
| *n*-BuLi | toluene | cyclohexanone | 67% | 65 : 35 | — |
| *n*-BuLi | toluene | $Me_3SiCl^a$ | 63%[b] | — | — |
| *i*-PrMgBr | hexane | PhCHO | 70% | >99 : <1 | 46 / 54 |
| *i*-PrMgBr | $Et_2O$ | PhCHO | 80% | >99 : <1 | 43 / 57 |
| *i*-PrMgBr | $Et_2O$ | *n*-$C_4H_9CHO$ | 72% | >99 : <1 | 11 / 89 |
| *i*-PrMgBr | $Et_2O$ | *t*-BuCHO | 58% | >99 : <1 | <1 / >99 |
| *i*-PrMgBr | $Et_2O$ | $PhCOCH_3$ | 88% | 92 : 8 | 25 / 75 |
| *i*-PrMgBr | $Et_2O$ | *n*-$C_9H_{19}COCH_3$ | 67% | >99 : <1 | 47 / 53 |
| *i*-PrMgBr | $Et_2O$ | cyclohexanone | 51% | 91 : 9 | — |
| $Et_2Zn$ | $Et_2O$ | PhCHO | 58% | >99 : <1 | 37 / 63 |
| $Et_2Zn$ | $Et_2O$ | *n*-$C_4H_9CHO$ | 63% | >99 : <1 | 13 / 87 |
| $Et_2Zn$ | $Et_2O$ | *t*-BuCHO | 44% | >99 : <1 | <1 / >99 |
| $Et_2Zn$ | $Et_2O$ | $PhCOCH_3$ | 61% | >99 : <1 | 14 / 86 |
| $Et_2Zn$ | $Et_2O$ | *n*-$C_9H_{19}COCH_3$ | 62% | >99 : <1 | 48 / 52 |
| $Et_2Zn$ | $Et_2O$ | cyclohexanone | 76% | >99 : <1 | — |

a) THF (1.0 ml) solution of $Me_3SiCl$ (1.1 mmol) was added.
b) Product is $Me_3SiCH{=}C{=}CH$-*n*-$C_5H_{11}$.

Several comments are worth noting. (1) Lithium-iodine exchange between allenyl iodide and *n*-BuLi was performed in hexane or toluene at −78 °C. The reaction at 0 °C gave complex mixtures upon treatment with carbonyl compounds. Meantime, metal-halogen exchange with *i*-PrMgBr or $Et_2Zn$ proceeded efficiently at 0 °C. Diethyl ether was a more suitable solvent than hexane or toluene in the case of *i*-PrMgBr or $Et_2Zn$. (2) The use of *i*-PrMgBr was essential for the successful metal-halogen exchange reaction. Treatment of 1-iodo-1,2-octadiene with MeMgI or *n*-BuMgBr followed by an addition of PhCHO gave the corresponding homopropargylic alcohols in only <3% or 8% yield. The adduct between Grignard reagent and PhCHO (PhCH(OH)Me or PhCH(OH)-*n*-Bu) was obtained in good yield and 1-iodo-1,2-octadiene was recovered (95% or 80%). (3) Whereas an addition of aldehyde to allenyllithium, derived from 1-iodo-1,2-octadiene and *n*-BuLi, provided homopropargylic alcohol almost exclusively, an addition of ketone such as acetophenone or 2-undecanone afforded a regioisomeric mixture of homopropargylic alcohol and allenyl alcohol. In contrast, allenylzinc reagent, generated from 1-iodo-1,2-octadiene and $Et_2Zn$, gave homopropargylic alcohols regioselectively upon treatment with not only aldehydes but also ketones. (4) Diastereoselectivities (ratio of *erythro/threo*) were not so high except with the reaction of *t*-BuCHO.

Diastereoselective synthesis of homopropargylic alcohols was achieved by the reaction of allenylzinc chloride derived from 1-lithio-1,2-octadiene and zinc chloride. Thus, lithiation of 1-iodo-1,2-octadiene in toluene with butyllithium at −78 °C followed by transmetalation with zinc chloride produced the corresponding allenylzinc reagent. An addition of aldehydes afforded *threo*-homopropargylic alcohols diastereoselectively (Table 3).[12] The selectivities are higher than those of the reaction with allenylethylzinc in Table 2. The high selectivities of the reaction with allenylzinc chloride might be attributed to lower reaction temperature compared to the reaction with latter reagent (−78 °C *vs* 0 °C). Whereas the reaction with allenylzinc chloride proceeded at −78 °C, the reaction with allenylethylzinc did not proceed at that temperature.

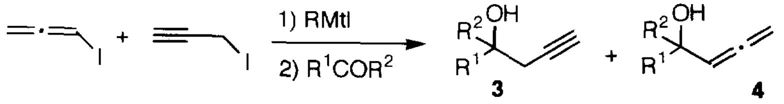
Table 3. Preparation of allenylzinc chloride by transmetalation and its reaction with aldehydes



| RCHO | Yield of Adduct (%) | Ratio of *erythro*:*threo* |
|---|---|---|
| *n*-$C_4H_9$CHO | 72 | 9 : 91 |
| *c*-$C_6H_{11}$CHO | 72 | 9 : 91 |
| *t*-BuCHO | 65 | <1 : >99 |

Treatment of an ethereal solution of a mixture of 1-iodo-1,2-propadiene and 3-iodo-1-propyne (2:1)[13] with *n*-BuLi or $Et_2Zn$ resulted in a formation of the corresponding organozinc reagent. An addition of various carbonyl compounds to the organometallic compound afforded the corresponding homopropargylic alcohols selectively (Table 4).[14]

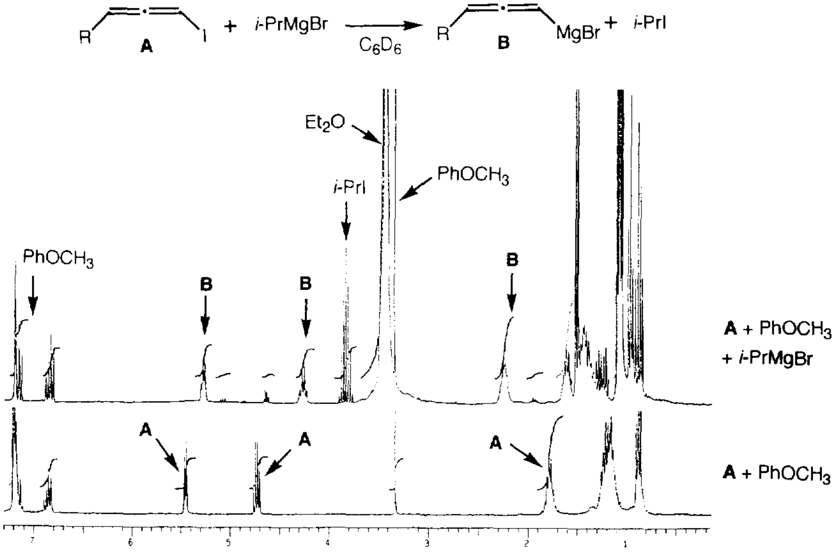
Table 4. Preparation and reaction of 1, 2-propadienyllithium and 1, 2-propadienylzinc



| Reaction Conditions | | | | | |
|---|---|---|---|---|---|
| RMtl | Temp | Solvent | $R^1COR^2$ | Yield of Adduct | Ratio of **3** : **4** |
| *n*-BuLi | −78 °C | toluene | PhCHO | 84% | >99 : <1 |
| *n*-BuLi | −78 °C | toluene | $n$-$C_4H_9CHO$ | 74% | 83 : 17 |
| *n*-BuLi | −78 °C | toluene | $PhCOCH_3$ | 97% | 89 : 11 |
| *n*-BuLi | −78 °C | toluene | cyclohexanone | 81% | 63 : 37 |
| $Et_2Zn$ | 0 °C | ether | PhCHO | 86% | >99 : <1 |
| $Et_2Zn$ | 0 °C | ether | $n$-$C_4H_9CHO$ | 78% | 96 : 4 |
| $Et_2Zn$ | 0 °C | ether | $PhCOCH_3$ | 57% | 96 : 4 |
| $Et_2Zn$ | 0 °C | ether | cyclohexanone | 50% | 97 : 3 |

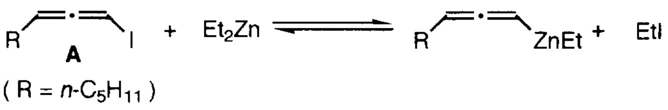
The formation of allenylmagnesium and allenylzinc reagents was examined by $^1H$ NMR spectra. The addition of isopropylmagnesium bromide (1.1 equiv) to a solution of 1-iodo-1,2-octadiene (**A**) in $C_6D_6$ containing anisole as an internal standard produced new signals at δ 4.28 (dt) and 5.28 (dt), which have been assigned to olefinic protons of allenylmagnesium compound. The peak of isopropyl iodide was also observed. On the other hand, the olefinic signals of **A** at δ 4.73 and 5.45 disappeared completely (Fig 1). The addition of benzaldehyde to the resulting mixture provided the corresponding homopropargylic alcohol as a single product in 80% yield.

Fig. 1



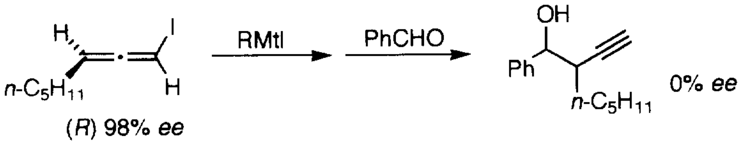
The addition of 1 equiv of diethylzinc to a solution of 1-iodo-1,2-octadiene (**A**) in $C_6D_6$ produced a signal of EtI and reduced the signals of olefinic protons of **A** at δ 4.73 and 5.45 to 60% of the original peaks. In contrast to the case of *i*-PrMgBr, no clear new peaks corresponding to allenylzinc or propargylzinc could be observed because of its polymeric nature.[15] The olefinic signals of **A** (50~60% of original peaks) remained even after being stirred for 2h at 25 °C. However, an addition of PhCHO to the mixture resulted in disappearance of olefinic protons of **A** and provided the corresponding homopropargylic alcohol in good yield. Thus, we are tempted to assume that equilibration between allenylzinc (and/or propargylzinc) and starting allenyl iodide has been established by the addition of $Et_2Zn$ to **A** (Scheme 2). Then, an addition of benzaldehyde, which reacts with allenylzinc but does not react with diethylzinc, shifted the equilibrium to right and eventually consumed the starting allenyl iodide to give the adduct in good yield.

**Scheme 2**



Transmetalation of optically active allenyl iodide was examined. Treatment of (*R*)-1-iodo-1,2-octadiene[16] (98% *ee*) with *n*-BuLi at –78 °C and then with PhCHO or $Me_3SiCl$ provided the corresponding homopropargylic alcohol PhCH(OH)-CH($n$-$C_5H_{11}$)-C≡CH (≈0% *ee*) or 1-trimethylsilyl-1,2-octadiene (≈0% *ee*) in 80% or 65% yield, respectively (Scheme 3). The complete loss of optical purity could be attributed to fast equilibrium between allenyllithium and propargyllithium. In the latter form, optical purity might be lost because of its stereochemical instability. The use of *i*-PrMgBr or $Et_2Zn$ in place of *n*-BuLi also resulted in a complete loss of optical purity. Thus, organometallics, prepared here via iodine-metal exchange, could exist as an equilibrium mixture of allenic and propargylic organometallic derivatives although only allenic magnesium species has been observed in NMR study.

**Scheme 3**



## Experimental

Distillation of the products was performed by the use of Kugelrohr (Büchi), and boiling points are indicated by air-bath temperature without correction. Melting points were obtained on a Yanako MP-50929 melting point apparatus and are uncorrected. $^1H$ NMR and $^{13}C$ NMR spectra were taken on a Varian GEMINI 300 spectrometer, $CDCl_3$ was used as a solvent, and chemical shifts being given in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Toluene, hexane, and diethyl ether were dried over a slice of sodium. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use.

*General Procedure for the Preparation of Alkenyllithium and Its Reaction with Carbonyl Compound.* Butyllithium (1.57 *M* hexane solution, 0.95 ml, 1.5 mmol) was added to a hexane (5.0 ml) solution of (*E*)-1-iodo-1-dodecene (0.29 g, 1.0 mmol) at 25 °C. The resulting solution was stirred at 25 °C for 15 min. Pentanal (0.10 g, 1.2 mmol) was added at 0 °C and the whole mixture was stirred for 10 min at 0 °C, then 10 min at 25 °C. Extractive workup followed by silica gel column purification gave (*E*)-6-heptadecen-5-ol (0.26 g) quantitatively.

*(E)-1-Phenyl-2-tridecen-1-ol* : Bp 140 °C (0.5 Torr, bath temp); IR (neat) 3322, 2952, 2922, 2850, 1454, 1379, 1072, 1030, 1007, 967, 754, 720 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.6 Hz, 3H), 1.21–1.40 (m, 16H), 1.85–1.86 (m, 1H), 2.05 (dt, *J* = 6.6, 6.6 Hz, 2H), 5.17 (d, *J* = 6.9 Hz, 1H), 5.65 (dd, *J* = 6.9, 15.3 Hz, 1H), 5.77 (dt, *J* = 15.3, 6.6 Hz, 1H), 7.25–7.39 (m, 5H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 22.7, 29.0, 29.2, 29.3, 29.5, 29.6, 31.9, 32.2, 75.3, 126.1, 127.5, 128.4, 132.1, 133.0. Found: C, 83.21; H, 11.03%. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02%.

*(E)-1-Cyclohexyl-2-tridecen-1-ol*: Bp 140 °C (0.5 Torr, bath temp); IR (neat) 3342, 2920, 2850, 1461, 1451, 1083, 1003, 969, 891, 720 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.6 Hz, 3H), 0.92–1.43 (m, 23H), 1.61–1.88 (m, 5H), 2.03 (dt, *J* = 6.6, 6.6 Hz, 2H), 3.77 (dd, *J* = 6.9, 6.9 Hz, 1H), 5.44 (ddt, *J* = 15.3, 6.9, 1.17 Hz, 1H), 5.62 (dt, *J* = 15.3, 6.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 22.7, 26.1, 26.5, 28.7, 28.8, 29.2, 29.3, 29.5, 29.6, 31.9, 32.3, 43.6, 77.8, 131.3, 133.2. Found: C, 81.20; H, 13.24%. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94%.

*(E)-1-(1-Hydroxycyclohexyl)-dodecene*: Bp 126 °C (0.5 Torr, bath temp); IR (neat) 3352, 2922, 2850, 1449, 1378, 1174, 1136, 1056, 1036, 969 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.6 Hz, 3H), 1.26–1.38 (m, 18H), 1.46–1.65 (m, 9H), 2.02 (dt, *J* = 6.3, 6.3 Hz, 2H), 5.55 (d, *J* = 15.7 Hz, 1H), 5.66 (dt, *J* = 15.7, 6.3 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 22.3, 22.7, 25.6, 29.1, 29.3, 29.5, 29.6, 31.9, 32.4, 38.1, 71.3, 128.3, 137.6. Found: C, 81.42; H, 13.10%. Calcd for $C_{18}H_{34}O$: C, 81.14; H, 12.86%.

*(Z)-6-Heptadecen-5-ol*: Bp 114 °C (0.5 Torr, bath temp); IR (neat) 3326, 2922, 2852, 1466, 1007, 721 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$) δ 0.86–0.93 (m, 6H), 1.22–1.62 (m, 23H), 2.04–2.10 (m, 2H), 4.43 (dt, *J* = 8.5, 6.5 Hz, 1H), 5.35 (ddt, *J* = 11.0, 8.5, 1.5 Hz, 1H), 5.49 (dt, *J* = 11.0, 7.4 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 14.0, 14.1, 22.7, 27.6, 27.7, 29.2, 29.3, 29.5, 29.6, 29.7, 31.9, 37.2, 67.7, 132.4, 132.5. Found: C, 80.00; H, 13.64%. Calcd for $C_{17}H_{34}O$: C, 80.24; H, 13.47%.

*(Z)-1-Cyclohexyl-2-tridecen-1-ol*: Bp 140 °C (0.5 Torr, bath temp); IR (neat) 3328, 3002, 2922, 2852, 1466, 1451, 1081, 1011, 891, 744, 720 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.6 Hz, 3H), 0.94–1.38 (m, 23H), 1.63–1.74 (m, 4H), 1.90–2.09 (m, 3H), 4.14 (dd, *J* = 8.7, 7.5 Hz, 1H), 5.37 (ddt, *J* = 11.2, 8.5, 1.3 Hz, 1H), 5.54 (dt, *J* = 11.2, 7.3 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 22.7, 26.0, 26.5, 27.8, 28.6, 28.8, 29.3, 29.5, 29.6, 29.7, 31.9, 43.9, 71.9, 130.9, 133.2. Found: C, 81.13; H, 13.18%. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94%.

*(Z)-2-Methyl-3-tetradecen-2-ol*: Bp 93 °C (0.5 Torr, bath temp); IR (neat) 3350, 2924, 2850, 1466, 1376, 1362, 1145, 954, 893, 721 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.6 Hz, 3H), 1.21–1.59 (m, 23H including δ 1.37 (s, 6H)), 2.31 (ddt, *J* = 7.0, 1.6, 7.0 Hz, 2H), 5.30 (dt, *J* = 11.8, 7.4 Hz, 1H), 5.48 (dt, *J* = 11.8, 1.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 22.7, 28.1, 29.3, 29.4, 29.6, 30.1, 31.1, 31.9, 71.6, 131.5, 136.6. Found: C, 79.30; H, 13.36%. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.36%.

*(Z)-1-(1-Hydroxycyclohexyl)-dodecene*: Bp 127 °C (0.5 Torr, bath temp); IR (neat) 3604, 3420, 2920, 2850, 1450, 1378, 1255, 1165, 1056, 961, 906, 720 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 0.88 (t, $J$ = 6.6 Hz, 3H), 1.23–1.67 (m, 27H), 2.34 (dt, $J$ = 6.9, 6.9 Hz, 2H), 5.38 (dt, $J$ = 11.7, 6.9 Hz, 1H), 5.46 (dt, $J$ = 11.7, 0.78 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 22.4, 22.7, 25.4, 28.5, 29.3, 29.4, 29.6, 30.1, 31.9, 39.2, 132.7, 135.9. Found: C, 81.12; H, 13.10%. Calcd for $C_{18}H_{34}O$: C, 81.14; H, 12.86%.

*(E)-6-Pentyl-6-dodecen-5-ol*: Bp 112 °C (0.5 Torr, bath temp); IR (neat) 3318, 2952, 2924, 2856, 1466, 1379, 1303, 1274, 1115, 1032, 866, 727 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 0.87–0.92 (m, 9H), 1.22–1.57 (m, 19H), 1.96–2.06 (m, 4H), 4.00 (t, $J$ = 6.6 Hz, 1H), 5.6 (t, $J$ = 7.5 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 22.5, 22.6, 22.7, 27.5, 28.2, 29.5, 29.7, 31.6, 32.4, 35.4, 126.9, 142.0. Found: C, 79.98; H, 13.60%. Calcd for $C_{17}H_{34}O$: C, 80.24; H, 13.47%.

*(E)-3-Pentyl-2-phenyl-3-nonen-2-ol:* Bp 124 °C (0.1 Torr, bath temp); IR (neat) 3442, 2954, 2924, 2856, 1493, 1466, 1459, 1448, 1378, 1061, 1028, 920, 907, 762, 699 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 0.80 (t, $J$ = 6.6 Hz, 3H), 0.90 (t, $J$ = 6.6 Hz, 3H), 1.11–1.44 (m, 11H), 1.57 (bs, 1H), 1.66 (s, 3H), 1.71–1.94 (m, 3H), 2.06 (dt, $J$ = 7.2, 7.2 Hz, 2H), 5.62 (t, $J$ = 7.2 Hz, 1H), 7.19–7.43 (m, 5H); $^{13}$C NMR ($CDCl_3$) δ 14.0, 14.1, 22.3, 22.6, 27.9, 28.6, 29.4, 29.5, 29.8, 30.2, 31.7, 32.5, 77.9, 125.5, 125.8, 126.6, 127.9, 144.2, 146.9. Found: C, 83.54; H, 11.34%. Calcd for $C_{20}H_{32}O$: C, 83.27; H, 11.18%.

*(E)-6-Trimethylsilyl-6-dodecene*: Bp 103 °C (20 Torr, bath temp); IR (neat) 2954, 2924, 2856, 1612, 1467, 1247, 835, 750, 686 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 0.05 (s, 9H), 0.90 (t, $J$ = 6.6 Hz, 6H), 1.25–1.39 (m, 12H), 2.04–2.11 (m, 4H), 5.70 (t, $J$ = 6.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ –1.1, 14.1, 22.56, 22.61, 28.4, 29.3, 29.7, 29.9, 31.7, 32.3, 140.3, 140.8. Found: C, 75.09; H, 13.37%. Calcd for $C_{15}H_{32}Si$: C, 74.91; H, 13.41%.

*2-Methylene-1-phenyl-1,3-propanediol:* Bp 140 °C (1.0 Torr, bath temp); IR (neat) 3308, 2922, 2870, 1493, 1453, 1020, 916, 760, 699 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 1.95 (bs, 1H), 2.70 (bs, 1H), 4.16 (d, $J$ = 13.1 Hz, 1H), 4.50 (d, $J$ = 13.1 Hz, 1H), 5.22 (d, $J$ = 0.9 Hz, 2H), 5.37 (s, 1H), 7.26–7.41 (m, 5H); $^{13}$C NMR ($CDCl_3$) δ 64.0, 76.3, 113.4, 126.2, 127.8, 128.5, 141.7, 149.2. Found: C, 72.92; H, 7.66%. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.36%.

*Preparation of Alkenylcuprate and Its Reaction with 2-Cyclohexen-1-one.* To a solution of CuCN (0.07 g, 0.75 mmol) in $Et_2O$ (5 ml) was added alkenyllithium at –78 °C, prepared from (*E*)-1-iodo-1-dodecene (0.29 g, 2.0 mmol) and butyllithium (1.5 mmol) in hexane. The mixture was stirred for 30 min and warmed to –20 °C. A solution of 2-cyclohexen-1-one (0.12 g, 1.2 mmol) in $Et_2O$ (2 ml) was added and the resulting mixture was allowed to warm to room temperature during 1 h. The mixture was poured into water and extracted with $Et_2O$ (20 ml×3). Concentration and purification by silica-gel column chromatography gave (*E*)-1-(3-Oxocyclohexyl)-1-dodecene (0.40 g) in 75% yield: Bp 134 °C (0.5 Torr, bath temp); IR (neat) 2918, 2852, 1715, 1460, 1449, 1423, 1345, 1315, 1222, 966 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 0.88 (t, $J$ = 6.6 Hz, 3H), 1.26–1.33 (m, 16H), 1.40–2.45 (m, 11H), 5.36 (dd, $J$ = 15.5, 5.5 Hz, 1H), 5.43 (dd, $J$ = 15.5, 5.7 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 22.7, 24.9, 29.1, 29.3, 29.4, 29.5, 29.6, 31.6, 31.9, 32.5, 41.3, 41.6, 47.7, 130.0, 132.9. Found: C, 81.67; H, 12.15%. Calcd for $C_{18}H_{32}O$: C, 81.75; H, 12.20%.

*1-Iodo-1,2-octadiene.* The title compound was prepared according to the procedure reported in the literature.[16]

*Standard Procedure for Preparation of Allenyllithium and Its Reaction with Electrophiles.* Reaction with pentanal is representative. To a solution of 1-iodo-1,2-octadiene (0.24 g, 1.0 mmol) in toluene (5 ml) was added butyllithium (1.58 *M* hexane solution, 0.76 ml, 1.2 mmol) at –78 °C. After being stirred for 5 min, pentanal (0.09 g, 1.1 mmol) in toluene (3 ml) was added and the mixture was stirred for 10 min at –78 °C and another 10 min at room temperature. The mixture was poured into 1 *M* HCl and extracted with ethyl acetate (20 ml×3). The combined organic layer were dried over $Na_2SO_4$ and concentrated *in vacuo*. Purification by silica-gel column chromatography gave 3-pentyl-1-octyn-4-ol (0.17 g) in 87% yield.

*Standard Procedure for Preparation of Allenylmagnesium and Allenylzinc Reagents and Their Reaction with Electrophiles.* Reaction with pentanal is representative. To a solution of 1-iodo-1,2-octadiene (0.24 g, 1.0 mmol) in $Et_2O$ (5 ml) was added $Et_2Zn$ (1.0 *M* hexane solution, 1.2 ml, 1.2 mmol) at 0 °C. After being stirred for 30 min, pentanal (0.09 g, 1.1 mmol) in $Et_2O$ (2 ml) was added and the mixture was stirred for another 30 min. To the reaction mixture, 1 *M* HCl was added carefully and extracted with ethyl acetate (20 ml×3). The combined organic layer were dried over $Na_2SO_4$ and concentrated *in vacuo*. Purification by silica-gel column chromatography gave 3-pentyl-1-octyn-4-ol (0.12 g) in 63% yield. The procedure for preparation and reaction of allenylmagnesium reagent is the same as that for allenylzinc reagent.

*2-Pentyl-1-phenyl-3-butyn-1-ol (47:53 diastereomeric mixture):* Bp 105 °C (0.5 Torr, bath temp); IR (neat) 3406, 3300, 3028, 2922, 2858, 2108, 1495, 1454, 1194, 1045, 914, 760, 701, 631 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.86 (t, $J$ = 6.9 Hz, 3H), 1.10–1.70 (m, 8H), 2.11 (d, $J$ = 2.4 Hz, 0.43H), 2.20 (s, 0.43H), 2.22 (d, $J$ = 2.4 Hz, 0.57H), 2.51 (s, 0.57H), 2.71 (m, 0.57H), 2.80 (m, 0.43H), 4.58 (d, $J$ = 6.6 Hz, 0.57H), 4.75 (d, $J$ = 5.7 Hz, 0.57H); $^{13}C$ NMR ($CDCl_3$) δ 13.86, 13.89, 22.36, 22.42, 26.81, 26.83, 29.46, 31.10, 31.37, 31.48, 39.97, 41.10, 71.88, 72.40, 75.66, 76.06, 84.21, 84.57, 126.61, 126.70, 127.87, 128.03, 128.19, 128.40, 141.61, 141.75. Found: C, 83.00; H, 9.42%. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32%.

*3-Pentyl-1-octyn-4-ol (16:84 diastereomeric mixture):* Bp 75 °C (0.5 Torr, bath temp); IR (neat) 3400, 3304, 2904, 2854, 2108, 1467, 1380, 1249, 1120, 901, 727, 626 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.90 (t, $J$ = 6.9 Hz, 3H), 0.92 (t, $J$ = 6.9 Hz, 3H), 1.20–1.60 (m, 8H), 1.67 (d, $J$ = 7.5 Hz, 0.84H), 2.12 (d, $J$ = 2.4 Hz, 0.16H), 2.14 (d, $J$ = 2.4 Hz, 0.84H), 2.41 (m, 0.84H), 2.51 (m, 0.16H), 3.50 (m, 0.84H), 3.58 (m, 0.16H); $^{13}C$ NMR ($CDCl_3$) δ 13.91, 22.43, 22.55, 27.08, 27.90, 29.85, 31.52, 33.23, 35.18, 38.85, 71.80, 72.98, 84.14. Found: C, 79.68; H, 12.38%. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32%.

threo-*2,2-Dimethyl-4-pentyl-5-hexyn-3-ol:* Bp 70 °C (0.5 Torr, bath temp); IR (neat) 3550, 3306, 2954, 2860, 2106, 1467, 1366, 1075, 1013, 752, 623 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.90 (t, $J$ = 6.9 Hz, 3H), 0.97 (s, 9H), 1.20–1.80 (m, 8H), 1.97 (d, $J$ = 10.2 Hz, 1H), 2.21 (d, $J$ = 2.4 Hz, 1H), 2.65 (m, 1H), 3.08 (d, $J$ = 10.2 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) δ 13.90, 22.43, 26.20, 26.90, 31.42, 33.75, 34.99, 35.95, 73.79, 80.01, 84.13. Found: C, 79.51; H, 12.30%. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32%.

*3-Pentyl-2-phenyl-4-pentyn-2-ol:* Bp 110 °C (0.5 Torr, bath temp); IR (neat) 3462, 3300, 3056, 2952, 2856, 2104, 1496, 1448, 1066, 851, 759, 699, 629 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.82 (t, $J$ = 6.9 Hz, 3H), 1.0–1.64 (m, 8H), 1.70 (s, 3H), 2.15 (s, 1H), 2.22 (d, $J$ = 2.4 Hz, 1H), 2.72 (ddd, $J$ = 2.4, 3.0, 11.4 Hz, 1H), 7.10–7.50 (m, 5H); $^{13}C$ NMR ($CDCl_3$) δ 13.86, 22.38, 27.37, 29.07, 29.75, 31.30, 44.70, 72.40, 75.25, 84.69, 125.07, 126.77, 128.14, 145.36. Found: C, 83.20; H, 9.83%. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63%.

*4-Methyl-3-pentyl-1-tridecyn-4-ol (50:50 diastereomeric mixture):* Bp 130 °C (0.5 Torr, bath temp); IR (neat) 3444, 3306, 2922, 2852, 2106, 1467, 1377, 1133, 930, 720, 623 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.88 (t,

$J$ = 6.9 Hz, 3H), 0.90 (t, $J$ = 6.9 Hz, 3H), 1.21 (s, 1.5H), 1.23 (s, 1.5H), 1.20–1.70 (m, 24.5H), 1.81 (s, 0.5H), 2.13 (d, $J$ = 2.7 Hz, 0.5H), 2.15 (d, $J$ = 2.4 Hz, 0.5H), 2.41 (m, 1H); $^{13}$C NMR ($CDCl_3$) δ 13.92, 13.98, 22.47, 22.57, 23.25, 23.42, 27.80, 28.83, 29.19, 29.22, 29.47, 29.53, 30.08, 31.55, 31.58, 31.80, 39.16, 39.64, 43.32, 43.49, 71.57, 71.87, 73.43, 73.69, 85.04, 85.26. Found: C, 81.42; H, 13.19%. Calcd for $C_{16}H_{22}O$: C, 81.36; H, 12.94%.

*1-(1-Pentyl-2-propynyl)cyclohexanol:* Mp 49–50 °C; IR (neat, before crystalization) 3444, 3306, 2928, 2856, 2104, 1450, 1380, 1265, 1153, 968, 622 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$) δ 0.90 (t, $J$ = 6.8 Hz, 3H), 1.10–1.70 (m, 19H), 2.15 (d, $J$ = 2.4 Hz, 1H), 2.35 (ddd, $J$ = 2.4, 2.4, 10.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 13.93, 21.73, 21.78, 22.46, 25.65, 27.73, 28.10, 31.57, 34.07, 35.05, 44.07, 71.89, 72.25, 85.06. Found: C, 80.48; H, 11.86%. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61%.

*1-(Trimethylsilyl)-1,2-Octadiene:* Bp 70 °C (8 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1939, 1467, 1380, 1249, 841, 758, 696 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$) δ 0.09 (s, 9H), 0.89 (t, $J$ = 6.9 Hz, 3H), 1.25–1.50 (m, 6H), 1.96 (ddt, $J$ = 3.9, 6.9, 6.9 Hz, 2H), 4.77 (dt, $J$ = 6.9, 6.9 Hz, 1H), 4.89 (dt, $J$ = 6.9, 3.9 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ -1.06, 13.95, 22.41, 27.73, 29.29, 31.31, 82.43, 83.47, 210.28. Found: C, 72.28; H, 12.36%. Calcd for $C_{15}H_{22}Si$: C, 72.44; H, 12.16%.

*Preparation of Allenylzinc Chloride and Its Reaction with aldehyde.* To a toluene solution of allenyllithium, prepared from 1-iodo-1,2-octadiene (0.24 g, 1.0 mmol) and butyllithium (1.2 mmol) was added a suspension of zinc chloride (0.16 g, 1.2 mmol) in THF (3 ml). After stirring 10 min, pentanal (0.09 g, 1.1 mmol) in toluene (2 ml) was added and stirred for another 10 min. Extractive workup followed by silica gel column purification gave 3-pentyl-1-octyn-4-ol (0.14 g, 9:91 diastereomeric mixture) in 72% yield.

*1-Phenyl-3-butyn-1-ol:* Bp 95°C (1.0 Torr, bath temp); IR (neat) 3288, 3028, 2910, 2114, 1420, 1189, 1050, 864, 755, 699, 631 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$) δ 2.08 (t, $J$ = 2.6 Hz, 1H), 2.38 (bs, 1H), 2.65 (dd, $J$ = 6.2, 2.6 Hz, 2H), 4.89 (t, $J$ = 6.2 Hz, 1H), 7.25–7.45 (m, 5H); $^{13}$C NMR ($CDCl_3$) δ 29.37, 70.93, 72.27, 80.64, 125.70, 127.95, 128.43, 142.38. Found: C, 82.04; H, 7.11%. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89%.

*1-Octyn-4-ol:* Bp 100 °C (18 Torr, bath temp); IR (neat) 3360, 3304, 2954, 2858, 2114, 1467, 1380, 1082, 1032, 844, 627 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$) δ 0.92 (t, $J$ = 6.9 Hz, 3H), 1.30–1.50 (m, 4H), 1.50–1.60 (m, 2H), 1.93 (S, 1H), 2.06 (t, $J$ = 2.6 Hz, 1H), 2.32 (ddd, $J$ = 2.6, 6.9, 16.8 Hz, 1H), 2.44 (ddd, $J$ = 2.6, 4.8, 16.8 Hz, 1H), 3.77 (m, 1H); $^{13}$C NMR ($CDCl_3$) δ 13.85, 22.46, 27.20, 27.62, 35.80, 69.84, 70.71, 80.93. Found: C, 75.95; H, 11.29%. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18%.

*2-Phenyl-4-pentyn-2-ol:* Bp 85 °C (1.0 Torr bath temp); IR (neat) 3288, 3026, 2976, 2930, 2114, 1495, 1447, 1376, 1273, 1098, 1069, 946, 852, 763, 698 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$) 1.65 (s, 3H), 2.06 (t, $J$ = 2.7 Hz, 1H), 2.40 (s, 1H), 2.69 (dd, $J$ = 16.8, 2.7 Hz, 1H), 2.78 (dd, $J$ = 16.8, 2.7 Hz, 1H), 7.20–7.50 (m, 5H); $^{13}$C NMR ($CDCl_3$) δ 28.24, 33.59, 70.85, 72.31, 79.54, 123.90, 126.33, 127.45, 145.53. Found: C, 82.43; H, 7.67%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%.

*1-(2-Propynyl)cyclohexanol:* Bp 105 °C (20 Torr, bath temp); IR (neat) 3402, 3300, 2930, 2854, 2112, 1449, 1356, 1266, 1152, 1077, 976, 873, 734, 623 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$) δ 1.20–1.35 (m, 1H), 1.40–1.85 (m, 10H), 2.08 (t, $J$ = 2.4 Hz, 1H), 2.37 (d, $J$ = 2.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ 22.11, 25.53, 32.80, 36.71, 70.33, 71.40, 80.60. Found: C, 78.09; H, 10.48%. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21%.

Financial support by the Ministry of Education, Science, Sports and Culture of Japan (Grant-in-Aid for Scientific Research No. 06403025, 05235106) are acknowledged.

## References and Notes

1. Wakefield, B. J. In *Organolithium Methods*; Academic: London, 1988; pp. 21–52.
2. Cahiez, G.; Bernard, D.; Normant, J. F. *Synthesis* **1976**, 245; Seebach, D.; Neumann, H. *Chem. Ber.* **1974**, *107*, 847; Neumann, H.; Seebach, D. *ibid.* **1978**, *111*, 2785; Lee, S. H.; Schwartz, J. *J. Am. Chem. Soc.* **1986**, *108*, 2445.
3. A part of this work was published in a communication: Yokoo, T.; Shinokubo, H.; Oshima, K.; Utimoto, K. *Synlett* **1994**, 645.
4. Conversion of (*E*)-alkenyl iodides into (*E*)-alkenyllithiums with *tert*-butyllithium in hexane has been reported. Peterson, M. A.; Polt, R. *Syn. Commun.* **1992**, 477.
5. Metal-halogen exchange reaction of 1-iodo-1-dodecene with *n*-BuLi proceeded six times faster than that of 1-bromo-1-dodecene.
6. The examination of $^1$H NMR of the $C_6D_6$ solution derived from (*E*)-1-iodo-1-dodecene and *n*-BuLi showed a presence of alkenyllithium ($\delta$ 2.5 (bs, 2H), 6.8 (bs, 1H), 7.0 (bs, 1H)) and *n*-BuI (2.76 (t, 2H)) in 1: 1 ratio.
7. Lipshutz, B. H.; Sengupta, S. *Org. Reactions* **41**, 135.
8. Yamamoto, H. in *Comprehensive Organic Synthesis*; Trost, B. M. Ed.; Pergamon Press: Oxford, **1991**; Vol. 2, p.81.
9. (a) Epsztein, R. in *Comprehensive Carbanion Chemistry*, Buncel, E.; Durst, T. Ed.; Elsevier, Amsterdam, 1984, part B, p.107; (b) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*, Wiley, New York, 1984; (c) S. R. Landor, S. R. Ed.; *The Chemistry of the Allenes*, Academic Press, New York, 1982; (d) Moreau, J.-L. in *The Chemistry of Ketenes, Allenes and Related Compounds*, Patai, S. Ed.; Wiley, New York, 1980, p.363; (e) Klein, J. in *The Chemistry of the Carbon-Carbon Triple Bond*, Patai, S. Ed.; Wiley, New York, 1978, p.343; (f) L. Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*, Elsevier, Amsterdam, 1981.
10. Preparation of allenic lithium reagents upon treatment of 1-bromo-1,2-undecadiene with *n*-BuLi in ether at –70 °C has been reported. Linstrumelle, G.; Michelot, D. *J. Chem. Soc. Chem. Commun.* **1975**, 561; Clinet, J.-C.; Linstrumelle, G. *Synthesis* **1981**, 875.
11. Transmetalation of allenyltrialkylstannanes with an alkyllithium has been reported. Suzuki, M.; Morita, Y; Noyori, R. *J. Org. Chem.* **1990**, *55*, 441.
12. Zweifel, G.; Hahn, G. *J. Org. Chem.* **1984**, 49, 4565.
13. Pure 1-iodo-1,2-propadiene could not be obtained. Treatment of propargyl bromide with sodium iodide in acetone followed by purification by distillation gave 2 : 1 mixture of 1-iodo-1,2-propadiene and propargyl iodide.
14. Recently selective preparation of homopropargylic and allenic alcohols using propargylsilanes and allenylsilans has been reported. Kobayashi, S; Nishio, K; *J. Am. Chem. Soc.* **1995**, *117*, 6392.
15. In hydrocarbon solvent, allenylzinc compound might be associated. An addition of $Et_2O$ to the $C_6D_6$ solution afforded clear new two olefinic peaks at $\delta$ 4.89 (dt) and 4.95 (m) which might be assigned to the corresponding allenylzinc compound.
16. Elsevier, C. J.; Meijer, T.; Tadema, G.; Stehouwer, P. M.; Bos, H. J. T.; Vermeer, P.; Runge, W. *J. Org. Chem.* **1982**, *47*, 2194.

(*Received in Japan* 28 *July* 1995; *accepted* 28 *August* 1995)