Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron 62 (2006) 7534–7539
Tetrahedron

Formal hydrochromination of alkynes under nickel catalysis. Regioselective reductive coupling of alkynes and aldehydes leading to allylic alcohols

Kazuhiko Takai,* Shuji Sakamoto, Takahiko Isshiki and Tatsuya Kokumai

Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan

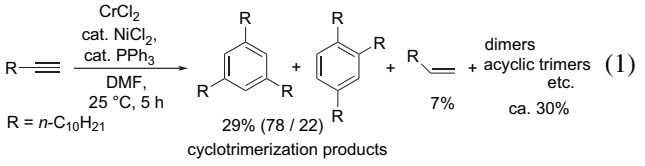
Received 7 November 2005; revised 11 April 2006; accepted 11 April 2006
Available online 15 June 2006

Dedicated to Professor Günther Wilke for his contribution to the field of organonickel chemistry

Abstract—Formal hydrochromation of an alkyne leading to a 1-substituted ethenylchromium reagent is accomplished by addition of the alkyne and water to a mixture of low-valent chromium(II), a catalytic amount of nickel(II), and triphenylphosphine in DMF.

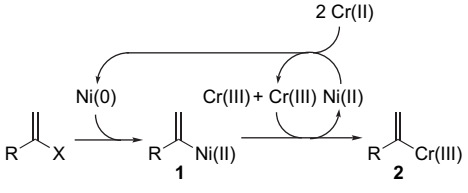
1. Introduction

Treatment of alkynes with a catalytic amount of a low-valent nickel species such as $NiBr_2$-magnesium or -zinc causes cyclotrimerization of the alkynes via nickelacylopropenes and nickelacyclopentadienes to give substituted benzenes.[1] However, when chromium(II) chloride is used as the reductant of a nickel(II) salt, the yield of the cyclotrimerization product decreases.[2] For example, treatment of 1-dodecyne with a mixture of $CrCl_2$, a catalytic amount of $NiCl_2$ and PPh_3 in DMF at 25 °C for 5 h gives the cyclotrimerization product in 29% yield (1,3,5-substituted benzene/1,2,4-substituted benzene = 78/22) and dodecenes in 7% yield (1-dodecene/2-dodecene = 86/14) along with a mixture of olefinic oligomers (dimers, trimers, tetramers, etc.) in ca. 30% combined yields (Eq. 1).



(1)

In separate studies carried out in 1986, we and Kishi reported independently the addition of alkenylchromium reagents to aldehydes to give allylic alcohols under nickel catalysis.[3] At that time, we assumed that the alkenylchromium(III) reagent **2** was generated by transmetallation from the alkenylnickel species **1** (Scheme 1).[3] Later, Hodgson showed that intramolecular insertion of a carbon–carbon triple bond into the generated arylnickel species with $CrCl_2$ and a catalytic amount of $NiCl_2$ occurred before the transmetallation to the alkenylchromium species.[4]



Scheme 1.

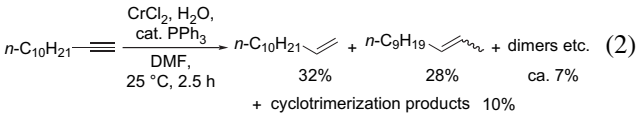
Because the chromium-mediated Barbier-type additions of alkenyl halides to aldehydes proceeded smoothly in the presence of a catalytic amount of a nickel salt, it was suggested that the transmetallation step from nickel to chromium proceeded smoothly under the reaction conditions. If this was the case, the amount of cyclotrimerization products of alkynes would decrease when a catalytic amount of low-valent nickel was generated in the presence of excess amounts of chromium salts because transmetallation from nickel to chromium occurs before formation of nickelacyclopentadienes. A decrease in the amount of cyclotrimerization products and the formation of the olefinic oligomers described in Eq. 1 suggested that the transmetallation from the alkenylnickel species to the corresponding chromium species proceeded in the reaction mixture to some extent.[5]

We then focused on the formation of dodecenes, which may have been derived by hydrolysis of the alkenylchromium species upon addition of water.[6] In order to examine this hypothesis, 8 equiv of water was added to a mixture of

* Corresponding author. E-mail: ktakai@cc.okayama-u.ac.jp

0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.04.105

$CrCl_2$, cat. $NiCl_2$, and cat. PPh_3 in DMF before addition of 1-dodecyne. Dodecenes were produced in 60% combined yields (1-dodecene/2-dodecene = 53/47) by stirring the mixture for 2.5 h (Eq. 2). When the reaction was quenched at 30 min, most of 1-dodecyne remained but the ratio of the formed dodecenes was 1-dodecene/2-dodecene = 90/10. Thus, the 2-dodecene was produced by isomerization of 1-dodecene in the reaction mixture.

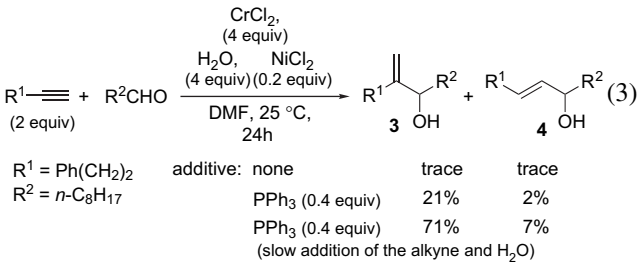


(2)

Nucleophilic carbon–carbon bond formation with organometallic compounds, except organoboron and -indium reagents, is usually conducted under water-free conditions. This is because organometallic compounds hydrolyze with a lot of water. However, the rate of hydrolysis of organochromium compounds is not very fast among the early transition metal compounds.[7] Therefore, the addition of an organochromium reagent can be accomplished without protecting the hydroxyl group of the substrate aldehyde in some cases,[8] and even a nucleophilic organochromium species can be generated by addition of a small aliquot of water.[9] As in Eq. 2, reduction of 1-dodecyne to 1-dodecene proceeded with $CrCl_2$ and water in the presence of a catalytic amount of $NiCl_2$ and PPh_3. If the two hydrogen atoms were introduced to 1-dodecyne with a different timing, i.e., one hydrogen atom was introduced later due to the hydrolysis of a carbon–chromium bond, new carbon–carbon bond formation could be established when the reaction was conducted in the presence of an aldehyde. In order to clarify this hypothesis, we examined the addition of a small amount of water to a mixture of an alkyne, $CrCl_2$, and catalytic amounts of $NiCl_2$ and PPh_3 in the presence of an aldehyde.

2. Results and discussion

To a stirred solution of chromium(II) chloride (4 equiv) and catalytic amounts of nickel(II) chloride (0.2 equiv) and PPh_3 (0.4 equiv) in DMF were added a solution of 4-phenyl-1-butyne (2 equiv) and nonanal (1 equiv) at 25 °C. A 1 M solution of water (2 equiv) in DMF was added slowly to the mixture at 25 °C over 2 h, and the mixture was stirred at the same temperature for an additional 4 h. After usual workup with water, the two desired allylic alcohols, 2-(2-phenylethyl)-1-undecen-3-ol (**3**) and (*E*)-1-phenyl-3-tridecen-5-ol (**4**) were obtained in a 23% combined yields (**3**/**4**=91/9, Eq. 3).[10]

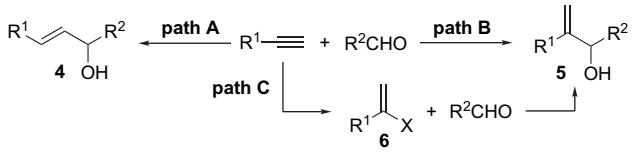


(3)

When the reaction was conducted without addition of PPh_3, a deposition of nickel(0) was observed, and most of the alkyne and the aldehyde were recovered; the two allylic alcohols **3** and **4** were detected after hydrolysis, although the combined yields were less than 3%. Addition of the phosphine ligand to the mixture was indispensable to prevent this deposition. Among those examined, triphenylphosphine was found to accelerate the reaction markedly. Effects of additives on the yields and regioselectivities of the reactions between 4-phenyl-1-butyne and nonanal were as follows: PBu_3, 14% (**3**/**4**=0/100); P(*o*-tolyl)$_3$, 16% (64/36); P(2-franyl)$_3$, 18% (78/22); P[3,5-$(CF_3)_2C_6H_3$]$_3$, 30% (90/10); P[2,6-$(MeO)_2C_6H_3$]$_3$, <5%.

The yield was also improved by slow addition of a mixture of the alkyne and water to a mixture of the aldehyde, chromium(II) chloride, nickel(II) chloride, and triphenylphosphine in DMF. For example, when a mixture of 4-phenyl-1-butyne (2 equiv) and water (2 equiv) in DMF was added at 25 °C over a period of 2 h to a mixture of nonanal (1 equiv), chromium(II) chloride (4 equiv), nickel(II) chloride (0.2 equiv), and triphenylphosphine (0.4 equiv) in DMF, a mixture of the two allylic alcohols was obtained in 78% yield (**3**/**4**= 91/9, Eq. 3). The 2-alkyl-substituted allylic alcohol **3** was produced selectively. Although the addition of water to the mixture was indispensable for the reaction, the yields of allylic alcohols decreased when an excess amount (16 equiv) of water was added.

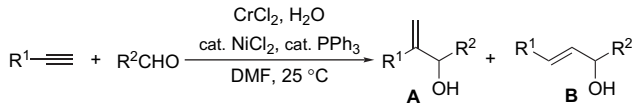
Addition of a metal-hydride species to a terminal alkyne generates two regioisomeric alkenylmetal compounds, which afford the corresponding allylic alcohols upon treatment with an aldehyde. Because hydroboration, -alumination, and -zirconation of a terminal alkyne generate the corresponding (*E*)-alkenylmetal compound, the 3-alkyl-substituted allylic alcohol **4** is produced selectively via these hydrometallation methods (Scheme 2, path A).[11,12] Recent reports on intermolecular coupling reactions promoted with Et_3B and a catalytic amount of nickel also produce the alcohol **4** regioselectively.[13] In contrast, it is not easy to prepare the 2-alkyl-substituted allylic alcohol **5** directly from a terminal alkyne and an aldehyde (path B). A two-step procedure via the 2-halo-1-alkene **6**[14] has been usually employed for this purpose (path C).[15] Therefore, the method using chromium(II) and water under nickel catalysis we report here is a direct approach for the preparation of the 2-substituted allylic alcohol **5** from a terminal alkyne and an aldehyde.

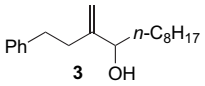
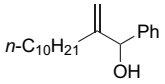
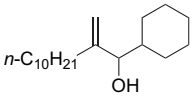
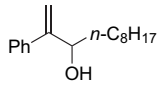
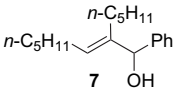
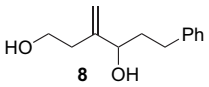
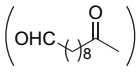
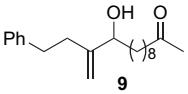
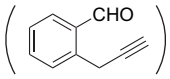
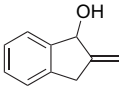


Scheme 2.

The results obtained with several kinds of alkynes and aldehydes are summarized in Table 1. Cyclotrimerization of the alkynes was also observed as a side reaction, thus, 2–3 equiv of the alkyne was employed to obtain good yields. Some additional interesting features are as follows: 2-substituted allylic alcohols were obtained in a selective manner except in the case of phenyl acetylene (entry 5). An internal alkyne, 6-dodecyne, also reacted with an aldehyde to give the corresponding allylic alcohol **7** in 60% yield although the reaction

Table 1. Coupling reactions between terminal alkynes and aldehydes[a]

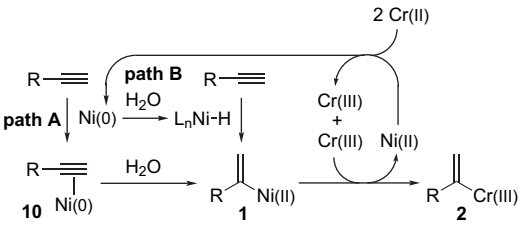


Entry	R^1	R^2	Time (h)	Major product	Yield (%)	**A/B**
1	$Ph(CH_2)_2$	*n*-C_8H_{17}	8	 **3**	82	95/5
2	$Ph(CH_2)_2$	*n*-C_8H_{17}	8	**3**	99[b]	95/5
3	*n*-$C_{10}H_{21}$	Ph	8		80[b]	94/6
4	*n*-$C_{10}H_{21}$	c-C_6H_{11}	8		79	90/10
5	Ph	*n*-C_8H_{17}	8		74	55/45
6	(6-Dodecyne)	Ph	24	 **7**	60[b]	
7	$HO(CH_2)_2$	$Ph(CH_2)_2$	8	 **8**	83[c]	>99/<1
8	$Ph(CH_2)_2$		8	 **9**	81	95/5
9			3		64	>99/<1

[a] Reaction was conducted on a 1.0 mmol scale. See typical procedure.
[b] Three mol of an alkyne, 6 mol of $CrCl_2$, 0.3 mol of $NiCl_2$, 0.6 mol of PPh_3, and 6 mol of water were used for per mole of an aldehyde. *E*/*Z* = 98/2.
[c] Three mol of water was used for per mole of an aldehyde.

proceeded slowly (entry 6). The alcohol **7** was produced almost exclusively, and the stereochemistry of the double bond of **7** proved to be the *E* configuration.[16] Since the coupling reaction is insensitive to a proton source, carbon–carbon bond formation could be accomplished without protecting the hydroxyl group (entry 7). In this case, one regioisomer **8** was produced exclusively, probably due to the coordination of the hydroxyl group to the nickel. A typical feature of the nucleophilic additions of organochromium reagents is their selective addition to aldehydes prior to ketone carbonyl groups.[7c,17] This was also observed in the reaction with a keto aldehyde (entry 8). An intramolecular reaction of 2-propargylbenzaldehyde proceeded under the similar reaction conditions to give 2-methyleneinden-1-ol in 64% yield selectively (entry 9).

There are two possibilities for the formation of the alkenylnickel species **1** from terminal alkynes (Scheme 3). In path A, a terminal alkyne coordinates to nickel(0) generated by the reduction of nickel(II) with 2 equiv of chromium(II), and a nickel–alkyne complex **10** is produced. A reaction of the complex **10** with water gives the alkenylnickel species **1**,[18] which transmetallates to yield the alkenylchromium reagent **2**. In path B, nickel(0) reacts immediately with water to give a nickel-hydride species. Addition of the nickel-hydride species to the terminal alkyne gives the alkenylnickel species **1**.[19]



Scheme 3.

Water is a typical proton source, but in this case it acts formally as a hydride anion source by reaction with low-valent metals.[20]

3. Experimental

3.1. General

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Dry, oxygen-free dimethylformamide (DMF) was purchased from Kanto Chemicals, Co. Column chromatography was performed with silica gel (200 mesh). Distillation of small amounts of products was performed with a Büchi Kugelrohr, and boiling points are indicated by an air bath temperature without correction. Preparative HPLC was performed on a Japan Analytical Industry LC-908 with JAI gel using toluene as an eluent. FTIR spectra were obtained on a Nicolet Protégé 460 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 instrument. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane using the δ scale. Low and high resolution of EI mass spectra were obtained with a capillary GC interfaced JEOL JMS-GCmate and JMS-700 MStation spectrometers, respectively. Elemental analyses were performed by the staff at the Elemental Analyses Center of Kyoto University.

3.2. Reaction of 1-dodecyne with $CrCl_2$ and water in the presence of a catalytic amount of $NiCl_2$ and PPh_3 (Eq. 2)

A mixture of $CrCl_2$ (0.37 g, 3.0 mmol) and a catalytic amount of $NiCl_2$ (19 mg, 0.15 mmol) and triphenylphosphine (0.77 g, 0.30 mmol) in DMF (4 mL) was stirred at 25 °C for 30 min. To the mixture was added a solution of water (0.22 g, 12 mmol) in DMF (2 mL) and the mixture was stirred for 15 min. To the greenish-yellow suspension was added a solution of 1-dodecyne (0.25 g, 1.5 mmol) in DMF (2 mL) over a period of 2 h, and the resulting mixture was stirred for an additional 30 min. The reaction mixture was poured into water (30 mL). The mixture was extracted with hexane (3×20 mL), and organic extracts were dried over anhydrous magnesium sulfate and concentrated. Purification by column chromatography on silica gel and preparative HPLC afforded dodecenes in 60% combined yields (0.15 g, 1-dodecene/2-dodecene = 53/47), trisubstituted benzenes in 10% combined yields (0.023 g, 1,3,5-substituted benzene/1,2,4-substituted benzene = 85/15), and a mixture of olefinic products containing 2,3-didecyl-1,3-butadiene and 2-decyl-1,3-tetradecadiene in ca. 7% yields.

3.3. Reductive coupling of alkynes and aldehydes. A general procedure (Table 1)

To a mixture of $CrCl_2$ (0.61 g, 5.0 mmol) and catalytic amounts of $NiCl_2$ (32 mg, 0.25 mmol) and triphenylphosphine (0.13 g, 0.50 mmol) in DMF (6 mL) was added a solution of an aldehyde (1.0 mmol) in DMF (4 mL) at 25 °C and the mixture was stirred for 10 min. A solution of a terminal alkyne (2.5 mmol) and water (72 μL) in DMF (10 mL) was added at 25 °C to the mixture over a period of 4 h. After stirring at 25 °C for an additional 4 h, the reaction mixture was poured into brine (30 mL). The mixture was extracted with ether (3×20 mL), and organic extracts were dried over anhydrous magnesium sulfate and concentrated. Purification by column chromatography on silica gel gave the desired coupling product.

3.3.1. 2-(2-Phenylethyl)-1-undecen-3-ol (3). Bp 145 °C (bath temp, 0.46 Torr); IR (neat): 3355, 3085, 3027, 2927, 2855, 1646, 1604, 1496, 1455, 1076, 1031, 901, 746, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J=6.9 Hz, 3H), 1.22–1.33 (m, 12H), 1.38–1.43 (m, 1H), 1.49–1.61 (m, 2H), 2.29 (dt, J=15.3, 8.0 Hz, 1H), 2.42 (dt, J=15.6, 8.0 Hz, 1H), 2.81 (t, J=8.1 Hz, 2H), 4.07 (s, 1H), 4.91 (d, J=1.2 Hz, 1H), 5.06 (s, 1H), 7.15–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 25.7, 29.3, 29.5, 29.6, 31.9, 32.9, 34.5, 35.5, 75.7, 109.9, 125.9, 128.3, 128.3, 142.0, 151.5. Anal. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 83.31; H, 11.27.

3.3.2. (*E*)-1-Phenyl-3-tridecen-5-ol (4).[21] IR (neat): 3337, 3108, 3086, 3027, 2954, 2855, 1604, 1496, 1454, 1377, 1304, 1131, 1030, 969, 746, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.89 (t, J=6.9 Hz, 3H), 1.23–1.31 (m, 12H), 1.34–1.37 (m, 1H), 1.41–1.53 (m, 2H), 2.36 (dt, J=7.8, 7.1 Hz, 2H), 2.70 (t, J=7.6 Hz, 2H), 4.00–4.05 (m, 1H), 5.47 (ddt, J=15.3, 7.1, 1.2 Hz, 1H), 5.67 (dt, J=15.3, 7.1 Hz, 1H), 7.17–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 25.4, 29.3, 29.5, 29.5, 31.9, 33.9, 35.6, 37.3, 73.1, 125.8, 128.3, 128.4, 130.9, 133.8, 141.7.

3.3.3. 2-Decyl-1-phenyl-2-propen-1-ol.[3a] IR (neat): 3364, 3085, 3063, 3029, 2925, 2853, 1648, 1603, 1493, 1454, 1377, 1190, 1025, 902, 842, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J=6.9 Hz, 3H), 1.19–1.31 (m, 14H), 1.34–1.43 (m, 2H), 1.79–1.88 (m, 2H), 1.95 (dt, J=15.6, 7.9 Hz, 1H), 4.98 (s, 1H), 5.16 (d, J=3.3 Hz, 1H), 5.26 (s, 1H), 7.28–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 27.8, 29.3, 29.4, 29.5, 29.55, 29.58, 31.8, 31.9, 77.3, 109.6, 126.7, 127.7, 128.4, 142.2, 151.2.

3.3.4. (*E*)-1-Phenyl-2-tridecen-1-ol.[22] IR (neat): 3347, 3103, 3082, 3060, 2926, 2855, 1599, 1494, 1465, 965, 748, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.86 (t, J=6.8 Hz, 3H), 1.21–1.28 (m, 14H), 1.34–1.41 (m, 2H), 1.90 (s, 1H), 2.03 (dt, J=7.2, 7.0 Hz, 2H), 5.14 (d, J=6.6 Hz, 1H), 5.63 (dd, J=15.3, 6.6 Hz, 1H), 5.74 (dt, J=15.3, 6.6 Hz, 1H), 7.23–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 29.1, 29.2, 29.3, 29.4, 29.6, 29.6, 31.9, 32.2, 75.2, 126.1, 127.4, 128.4, 132.2, 132.9, 143.4.

3.3.5. 1-Cyclohexyl-2-decyl-2-propen-1-ol. Bp 120 °C (bath temp, 0.45 Torr); IR (neat): 3398, 2924, 2852, 1645, 1465, 1450, 1378, 1306, 1261, 1082, 1021, 897, 803, 735, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J=6.8 Hz, 3H), 0.92–1.05 (m, 1H), 1.11–1.29 (m, 18H), 1.41–1.50 (m, 5H), 1.63–1.67 (m, 1H), 1.71–1.79 (m, 2H), 1.88–1.96 (m, 2H), 2.06 (dt, J=15.9, 7.9 Hz, 1H), 3.77 (d, J=6.9 Hz, 1H), 4.88 (d, J=3.0 Hz, 1H), 4.95 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 26.1, 26.3, 26.5, 28.0, 28.1, 29.4, 29.59, 29.63, 29.63, 29.7, 29.9, 31.2, 31.9, 41.0, 80.7, 110.3, 151.0. Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.43; H, 13.08.

3.3.6. (*E*)-1-Cyclohexyl-2-tridecen-1-ol. IR (neat): 3371, 2925, 2853, 1669, 1464, 1450, 1378, 1306, 1261, 1084, 1004, 969, 892, 721, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J=6.7 Hz, 3H), 0.91–1.01 (m, 1H), 1.14–1.43 (m, 21H), 1.64–1.77 (m, 4H), 1.86 (d, J=12.6 Hz, 1H), 2.03 (dt, J=7.2, 7.1 Hz, 2H), 2.17 (s, 1H), 3.76 (t, J=6.9 Hz, 1H), 5.44 (dd, J=15.3, 7.5 Hz, 1H), 5.60 (dt, J=15.3, 7.1 Hz,

1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 26.07, 26.15, 26.6, 28.7, 28.8, 29.16, 29.23, 29.3, 29.5, 29.60, 29.61, 31.9, 32.3, 43.7, 77.7, 131.4, 133.1. Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.20; H, 13.12.

3.3.7. 2-Phenyl-1-undecen-3-ol.[23] IR (neat): 3415, 3080, 3056, 2924, 2854, 1630, 1574, 1494, 1465, 1378, 1131, 1064, 1027, 908, 777, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.87 (t, J=6.9 Hz, 3H), 1.19–1.28 (m, 11H), 1.42–1.63 (m, 3H), 1.75 (s, 1H), 4.60–4.64 (m, 1H), 5.30 (s, 1H), 5.35 (s, 1H), 7.30–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 25.6, 29.2, 29.4, 29.5, 31.8, 36.0, 73.9, 112.5, 126.9, 127.5, 128.3, 140.1, 152.2.

3.3.8. (*E*)-1-Phenyl-1-undecen-3-ol.[24] IR (neat): 3347, 3103, 3082, 3026, 2926, 2855, 1599, 1494, 1465, 965, 748, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J=6.6 Hz, 3H), 1.23–1.45 (m, 12H), 1.55–1.71 (m, 3H), 4.27 (dd, J=6.6, 6.3 Hz, 1H), 6.21 (dd, J=15.9, 6.6 Hz, 1H), 6.56 (d, J=15.9 Hz, 1H), 7.21–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 25.4, 29.2, 29.5, 29.6, 31.8, 37.4, 73.1, 126.4, 127.6, 128.5, 130.1, 132.6, 136.8.

3.3.9. (*E*)-2-Pentyl-1-phenyl-2-octen-1-ol (7).[16] IR (neat): 3357, 3089, 3062, 2955, 2927, 2857, 1493, 1455, 1378, 1084, 1008, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.83 (t, J=6.9 Hz, 3H), 0.90 (t, J=6.9 Hz, 3H), 1.14–1.15 (m, 12H), 1.77 (d, J=3.3 Hz, 1H), 1.77–1.86 (m, 1H), 1.93–2.03 (m, 1H), 2.07 (dt, J=7.3, 7.2 Hz, 2H), 5.16 (d, J=2.7 Hz, 1H), 5.61 (t, J=7.2 Hz, 1H), 7.24–7.37 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.0, 14.1, 22.4, 22.6, 27.6, 27.7, 29.2, 29.5, 31.7, 32.1, 78.2, 126.5, 127.3, 127.3, 128.2, 141.2, 142.8.

3.3.10. 3-Methylene-6-phenyl-hexane-1,4-diol (8). IR (neat): 3353, 3085, 3026, 2927, 2862, 1645, 1603, 1496, 1454, 1320, 1045, 908, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.84–1.98 (m, 2H), 2.29–2.33 (m, 2H), 2.43 (ddd, J=14.0, 8.1, 6.0 Hz, 1H), 2.64 (ddd, J=13.8, 9.1, 6.8 Hz, 1H), 2.74 (ddd, J=13.9, 9.4, 6.4 Hz, 2H), 3.72 (ddd, J=10.4, 8.0, 4.7 Hz, 1H), 3.82 (dt, J=10.5, 5.4 Hz, 1H), 4.13 (t, J=5.4 Hz, 1H), 4.98 (d, J=1.2 Hz, 1H), 5.12 (s, 1H), 7.17–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 32.0, 34.8, 37.1, 62.4, 74.9, 113.7, 125.9, 128.41, 128.43, 141.8, 148.8. Elemental analysis was conducted with a trimethylsilyl ether of **8** [bp 60 °C (bath temp, 1.3 Torr)]. Anal. Calcd for $C_{19}H_{34}O_2Si_2$: C, 65.08; H, 9.77. Found: C, 65.04; H, 9.85.

3.3.11. 11-Hydroxy-12-(2-phenylethyl)-12-tridecen-2-one (9). IR (neat): 3428, 3063, 3027, 2929, 2855, 1713, 1646, 1604, 1496, 1454, 1360, 1167, 900, 748, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.24–1.28 (m, 12H), 1.51–1.58 (m, 3H), 2.13 (s, 3H), 2.29 (dt, J=15.3, 7.9 Hz, 1H), 2.41 (t, J=7.3 Hz, 2H), 2.42 (dt, J=15.3, 8.0 Hz, 1H), 2.80 (t, J=8.2 Hz, 2H), 4.05–4.09 (m, 1H), 4.92 (d, J=1.2 Hz, 1H), 5.07 (s, 1H), 7.17–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 23.8, 25.7, 29.1, 29.3, 29.4, 29.5, 29.8, 32.9, 34.5, 35.5, 43.8, 75.6, 109.9, 125.9, 128.3, 128.3, 142.0, 151.5, 209.3. Elemental analysis was conducted with a trimethylsilyl ether of **9** [bp 155 °C (bath temp, 0.34 Torr)]. Anal. Calcd for $C_{24}H_{40}O_2Si$: C, 74.17; H, 10.37. Found: C, 74.06; H, 10.56.

3.3.12. (*E*)-11-Hydroxy-15-phenyl-12-pentadecen-2-one. IR (neat): 3409, 3026, 2928, 2854, 1715, 1496, 1454, 1361, 969, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.20–1.31 (m, 12H), 1.43–1.58 (m, 3H), 2.13 (s, 3H), 2.36 (dt, J=7.7, 7.8 Hz, 2H), 2.41 (t, J=7.5 Hz, 2H), 2.70 (dd, J=8.1, 7.2 Hz, 2H), 4.01 (dt, J=6.6, 6.6 Hz, 1H), 5.46 (dd, J=15.3, 6.9 Hz, 1H), 5.66 (dt, J=15.3, 6.6 Hz, 1H), 7.16–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 23.8, 25.3, 29.1, 29.30, 29.35, 29.4, 29.8, 33.9, 35.6, 37.2, 43.8, 73.0, 125.8, 128.3, 128.4, 130.9, 133.9, 141.7, 209.3. Elemental analysis was conducted with a trimethylsilyl ether of (*E*)-11-hydroxy-15-phenyl-12-pentadecen-2-one [bp 150 °C (bath temp, 0.3 Torr)]. Anal. Calcd for $C_{24}H_{40}O_2Si$: C, 74.17; H, 10.37. Found: C, 74.29; H, 10.42.

3.3.13. 2-Methyleneindan-2-ol. IR (nujol): 3306, 3072, 1662, 1610, 1586, 1317, 1250, 1204, 1174, 1037, 895, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.81 (d, J=9.0 Hz, 1H), 3.62 (d, J=20.0 Hz, 1H), 3.70 (d, J=20.1 Hz, 1H), 5.29 (dd, J=4.1, 1.9 Hz, 1H), 5.49 (d, J=9.0 Hz, 1H), 5.50 (dd, J=4.1, 2.1 Hz, 1H), 7.24–7.51 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 36.5, 76.5, 110.4, 124.7, 124.9, 127.1, 128.6, 140.8, 144.0, 152.8; EI MS m/z (%): 146 (M^+, 100), 145 (61), 131 (66), 118 (28), 115 (47), 91 (25). HRMS (EI) m/z calcd for (M^+) $C_{10}H_{10}O$ 146.0732, found 146.0732.

Acknowledgements

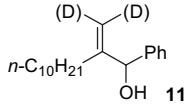
This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Culture, Sports, Science, and Technology of Japan and by the Nagase Science and Technology Foundation.

References and notes

1. (a) Saito, S. *Modern Organonickel Chemistry*; Tamaru, Y., Ed.; Wiley-VCH: Weinheim, 2005; pp 171–204; (b) Reppe, W.; Schweckendiek, W. J. *Justus Liebigs Ann. Chem.* **1948**, *560*, 104–116; (c) Alphonse, P.; Moyen, F.; Mazerolles, P. *J. Organomet. Chem.* **1988**, *345*, 209–216.
2. Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5268–5270.
3. (a) Takai, K.; Tagashira, M.; Kuroda, T.; Oshima, K.; Utimoto, K.; Nozaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 6048–6050; (b) Jin, H.; Uenishi, J.-i.; Christ, W. J.; Kishi, Y. *J. Am. Chem. Soc.* **1986**, *108*, 5644–5646.
4. Hodgson, D. M.; Wells, C. *Tetrahedron Lett.* **1994**, *35*, 1601–1604.
5. For transmetallation from zirconium to chromium, see: Takahashi, T.; Liu, Y.; Chaki, S.; Nakajima, K.; Kanno, K.-i. *J. Am. Chem. Soc.* **2005**, *127*, 11928–11929.
6. There is a possibility of hydrolysis with a trace amount of water in the reaction mixture.
7. (a) Hanson, J. R.; Premuzic, E. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 247–252; (b) Espenson, J. H. *Acc. Chem. Res.* **1992**, *25*, 222–227; (c) Wessjohann, L. A. *Synthesis* **1999**, 1–36.
8. Kauffmann, T.; Abeln, R.; Wingbermühle, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 729–730.
9. Takai, K.; Toratsu, C. *J. Org. Chem.* **1998**, *63*, 6450–6451; See also a review on water-accelerated organic transformations: Ribe, S.; Wipf, P. *Chem. Commun.* **2001**, 299–307.
10. Takai, K.; Sakamoto, S.; Isshiki, T. *Org. Lett.* **2003**, *5*, 653–655.
11. For representative examples using hydrozirconation, see: (a) Maeta, H.; Hashimoto, T.; Hasegawa, T.; Suzuki, K.

Tetrahedron Lett. **1992**, *33*, 5965–5968; (b) Wipf, P.; Xu, W. *Tetrahedron Lett.* **1994**, *35*, 5197–5200.

12. The reactivity of the alkenylboron and -aluminum species towards carbonyl compounds is low even when they are converted to the corresponding ate complexes. Thus, the alkenylboron and -aluminum species are usually converted to the corresponding halides with electrophilic sources of halides (iodine or *N*-bromosuccinimide), and metallated. (a) Brown, H. C.; Bowman, D. H.; Misumi, S.; Unni, M. K. *J. Am. Chem. Soc.* **1967**, *89*, 4531–4532; (b) Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 2753–2754.
13. (a) Oblinger, E.; Montgomery, J. *J. Am. Chem. Soc*. **1997**, *119*, 9065–9066; (b) Huang, W.-S.; Chan, J.; Jamison, T. F. *Org. Lett.* **2000**, *2*, 4221–4223.
14. Kamiya, N.; Chikami, Y.; Ishii, Y. *Synlett* **1990**, 675–676; See also: Takai, K.; Sakogawa, K.; Kataoka, Y.; Oshima, K.; Utimoto, K. *Org. Synth.* **1995**, *72*, 180–188.
15. For representative examples, see: Rowley, M.; Tsukamoto, M.; Kishi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2735–2737; MacMillan, D. W. C.; Overman, L. E. *J. Am. Chem. Soc.* **1995**, *117*, 10391–10392; Taylor, R. E.; Chen, Y. *Org. Lett.* **2001**, *3*, 2221–2224.
16. Takai, K.; Kataoka, Y.; Utimoto, K. *J. Org. Chem.* **1990**, *55*, 1707–1708; Inoue, A.; Kitagawa, K.; Shinokubo, H.; Oshima, K. *J. Org. Chem.* **2001**, *66*, 4333–4339.
17. For reviews on organochromium reagents, see: (a) Takai, K.; Utimoto, K. *J. Synth. Org. Chem. Jpn.* **1988**, *46*, 66–77; (b) Fürstner, A. *Chem. Rev.* **1999**, *99*, 991–1046; (c) Takai, K. *Org. React.* **2004**, *64*, 253–612. see also Ref. 7c.
18. Bennett, M. A.; Castro, J.; Edwards, A. J.; Kopp, M. R.; Wenger, E.; Willis, A. C. *Organometallics* **2001**, *20*, 980–989.
19. In order to obtain more information for the reaction, we used a deuterated terminal allylic alcohol **11** for the coupling reaction. Deuterium was incorporated in both cis and trans positions in a 1:1 ratio.



11

20. (a) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 6777–6784; (b) Trost, B. M. *Chem.—Eur. J.* **1998**, 2405–2412.
21. Inomata, K.; Igarashi, S.; Mohri, M.; Yamamoto, T.; Kinoshita, H.; Kotake, H. *Chem. Lett.* **1987**, 707–710.
22. Kitagawa, K.; Inoue, A.; Shinokubo, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 2481–2483.
23. Takai, K.; Kimura, K.; Kuroda, T.; Hiyama, T.; Nozaki, H. *Tetrahedron Lett.* **1983**, *24*, 5281–5284.
24. Vettel, S.; Vaupel, A.; Knochel, P. *J. Org. Chem.* **1996**, *61*, 7473–7481.