hydrogen evolution ceased. The resulting solution was kept with stirring for 1 h, filtered trough a pad of Celite, and evaporated to afford a residue that was chromatographed (hexane–ethyl acetate (19:1) to give **6** as a colorless oil (14.1 g, 84% from **4**): $[\alpha]^{22}_D$ = +17.1 (*c* 0.90, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.20 (t, 6 H, 2 Me, J = 7.4 Hz), 1.29 (s, 3 H, Me), 1.35 (s, 3 H, Me), 1.69–1.79 (m, 2 H, 2 H-4), 1.81 (ddd, 1 H, H-2a, $J_{1,2a}$ = 8.5 Hz, $J_{2a,3}$ = 2.9 Hz, $J_{2a,2b}$ = 11.8 Hz), 1.94 (ddd, 1 H, H-2b, $J_{1,2b}$ = 5.9 Hz, $J_{2b,3}$ = 9.0 Hz, $J_{2a,2b}$ = 11.8 Hz), 2.54–2.73 (m, 4 H, 2 SCH_2), 2.99 (b d, 1 H, OH, J = 4.4 Hz), 3.55 (t, 1 H, H-6a, $J_{6a,6b}$ = $J_{5,6a}$ = 7.45 Hz), 3.99 (dd, 1 H, H-1, $J_{1,2a}$ = 8.5 Hz, $J_{1,2b}$ = 5.9 Hz), 4.04 (dd, 1 H, H-6b, $J_{6a,6b}$ = 7.45 Hz, $J_{5,6b}$ = 6.1 Hz), 4.06–4.09 (m, 1 H, H-3), 4.11–4.32 (m, 1 H, H-5); ^{13}C NMR ($CDCl_3$) δ 14.2, 14.3, 24.0, 24.2, 25.6, 26.8, 40.4, 43.6, 48.5, 53.2, 67.2, 69.5, 73.5, 108.7. Anal. Calcd for $C_{13}H_{26}O_3S_2$: C, 53.03; H, 8.90; S, 21.77. Found: C, 53.92; H, 8.82; S. 21.54.

2,4-Dideoxy-5,6-*O*-isopropylidene-3-(*p*-nitrobenzoyl)-D-**allose Diethyl Dithioacetal (7).** To a stirred solution of **6** (5.2 g, 17.69 mmol), PPh_3 (32.4 g, 123.8 mmol), and PNBOH (20.7 g, 123.8 mmol) in dry toluene (350 mL) was added a solution of DEAD (19.5 mL, 123.8 mmol) in toluene (60 mL). The reaction mixture was stirred for 1 h at rt, the suspension filtered, the solution concentrated in vacuo, and the residue chromatographed (hexane–ethyl acetate (95:5) to yield **7** (4.91 g, 61%) as a colorless oil: $[\alpha]^{22}_D$ = −14.8 (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.15 (t, 3 H, Me, J = 7.4 Hz), 1.17 (t, 3 H, Me, J = 7.4 Hz), 1.20 (s, 3 H, Me), 1.29 (s, 3 H, Me), 1.87 (dt, 1 H, H-4a, $J_{4a,5}$ = $J_{3,4a}$ = 4.7 Hz, $J_{4a,4b}$ = 14.5 Hz), 2.15–2.96 (m, 2 H, H-2a), 2.29 (ddd, 1 H, H-2b, $J_{1,2b}$ = 6.2 Hz, $J_{2b,3}$ = 8.4 Hz, $J_{2a,2b}$ = 14.7 Hz), 2.47–2.66 (m, 4 H, 2 SCH_2), 3.51 (t, 1 H, H-6a, $J_{6a,6b}$ = $J_{5,6a}$ = 5.9 Hz), 3.81 (dd, 1 H, H-1, $J_{1,2a}$ = 8.6 Hz, $J_{1,2b}$ = 6.2 Hz), 4.02 (dd, 1 H, H-6b, $J_{6a,6b}$ = 12.1 Hz, $J_{5,6b}$ = 5.9 Hz), 4.10–4.17 (m, 1 H, H-5), 5.50–5.58 (m, 1 H, H-3), 8.14– 8.28 (m, 4 H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 14.3, 14.4, 23.9, 24.0, 25.6, 26.9, 37.8, 40.5, 47.5, 69.4, 71.9, 72.7, 109.1, 123.5, 130.7, 130.8, 135.7, 164.1. Anal. Calcd for $C_{20}H_{29}O_6S_2N$: C, 54.16; H, 6.59; S, 14.46; N, 31.6. Found: C, 52.92; H, 6.47; S, 14.28; N, 3.02.

Methyl 2,4-Dideoxy-3-(*p*-nitrobenzoyl)-D-**allopyranosides (2).** A solution of **7** (4.0 g, 9 mmol) in MeOH (200 mL) was added to a suspension of red mercury oxide (3.9 g, 18 mmol) and $BF_3{\cdot}Et_2O$ (4.5 mL, 36 mmol) in MeOH (80 mL) and stirred for 5 h, after which time Et_2O was added and the precipitated salts were filtered. The resulting solution was washed with saturated $NaHCO_3$, water, and brine, dried ($MgSO_4$), and evaporated in vacuo and the residue chromatographed (hexane–ethyl acetate (6:4)) to afford **2** (α/β mixture (1:1)) as a colorless oil (2.6 g, 95%): ^1H NMR ($CDCl_3$) δ (selected data) 4.78 (dd, 0.5 H, $J_{1,2ax}$ = 9.6 Hz, $J_{1,2eq}$ = 2.2 Hz, H-1β) 4.85 (d, 0.5 H, $J_{1,2}$ = 4.0 Hz, H-1α), 5.39 (quint, 0.5 H, J = 3.16 Hz, H-3β), 5.57 (quint, 0.5 H, J = 3.16 Hz, H-3α); ^{13}C NMR ($CDCl_3$) δ 31.5, 31.8, 33.6, 36.5, 56.3, 57.6, 65.1, 66.4, 66.6, 68.5, 71.2, 72.7, 98.7 (C-1, β-anomer), 100.5 (C-1, α-anomer), 124.5, 124.7, 131.7, 131.8, 137.2, 137.5, 151.5, 151.7, 164.6, 165.1. Anal. Calcd for $C_{14}H_{17}O_7N$: C, 54.02; H, 5.50; N, 4.50. Found: C, 53.89; H, 5.37; N, 4.32.

Registry No. α-**2**, 138386-35-3; β-**2**, 138386-40-0; **3**, 4258-02-0; **4**, 138386-36-4; **5**, 138386-37-5; **6**, 138386-38-6; **7**, 138386-39-7; PNBOH, 62-23-7; D-glucose, 50-99-7.

Selective Reduction of Alkynes to (*Z*)-Alkenes via Niobium- or Tantalum-Alkyne Complexes

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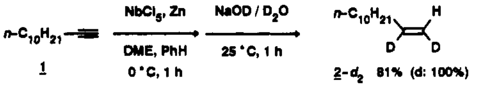
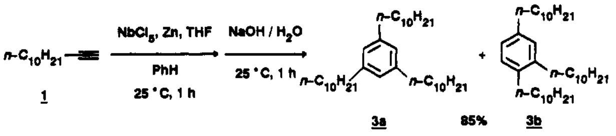
Because the rates of hydrogenation of double and triple bonds do not differ appreciably, several catalysts for partial hydogenation of alkynes leading to (*Z*)-alkenes have been developed.[1] In contrast to hydrogenation, partial reduction of alkynes with sodium in liquid ammonia gives (*E*)-alkenes predominantly.[1] In 1982, we introduced low-valent niobium prepared by the reduction of $NbCl_5$ with $NaAlH_4$ and used it for some reductions, i.e. the pinacol-type reductive coupling of aldehydes or ketones and reduction of alkynes.[2] In the latter reaction with internal alkynes, high (*Z*)-alkene preference was recognized compared to $TiCl_4$–$LiAlH_4$ reagent.[3] This observation suggests the possibility of two reaction pathways. One possibility is the formation of a niobium–alkyne complex[4,5] as an intermediate. Pedersen isolated a one-to-one complex of niobium and an alkyne which is produced by treatment of the alkyne with $NbCl_3$(DME).[5] Another possibility is a hydrometalation pathway by Nb–H species.[6] However, quenching of the reaction mixture of an internal alkyne with D_2O did not give a deuterated olefin. Thus, we reexamined our previous niobium chemistry under the conditions using a reducing agent having no hydride source.[4,7]

In contrast to the previous $NbCl_5$–$NaAlH_4$ system,[2] a combination of $NbCl_5$ and zinc was found to give a vicinal dideuterated olefin after quenching the reaction mixture with NaOD–D_2O.[8,9] Treatment of 1-dodecyne with the combination of 4 equiv of $NbCl_5$ and 6 equiv of zinc in a solvent of DME–benzene (1:1) at 0 °C for 1 h followed by addition of alkaline D_2O afforded (*E*)-1,2-dideuterio-1-dodecene (**2-*d*$_2$**) in 81% yield (eq 1). The reaction course changed dramatically when a mixed solvent of benzene and THF (8 molar quantity of $NbCl_5$) was employed. Cyclotrimerization products of 1-dodecyne, a mixture of regioisomers **3a** and **3b**, was produced in 85% combined yields (eq 2).[4a,10]



(1)



(2)

Aluminum powder was also effective for the reduction of $NbCl_5$. Ultrasonic irradiation to a mixture of $NbCl_5$ and

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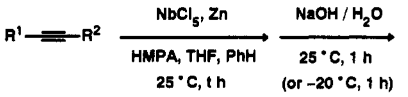
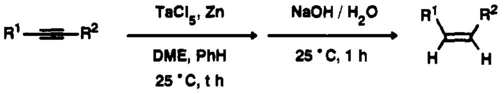
Table I. Reduction of Alkynes to (*Z*)-Alkenes by Means of a $NbCl_5$–Zn System[a]



run	R^1	R^2	t/h	yield/%[b]	Z/E[c]
1	n-$C_{10}H_{21}$	H	1	72[d]	–
2	Ph	H	2	81[d,e]	–
3	n-C_5H_{11}	n-C_5H_{11}	20	74	>99/<1
4	$-(CH_2)_{10}-$		7	82	>99/<1[f]
5	Ph	n-C_6H_{13}	20	86[g]	>99/<1[f]
6	c-C_6H_{11}	n-C_6H_{13}	40	81[g]	97/3
7	t-Bu	n-C_7H_{15} (**4**)	40	62[g]	97/3[h,i]
8	Me_3Si	n-$C_{10}H_{21}$ (**5**)	40	81[g]	96/4[f,h,j]

[a] The alkyne (1.0 mmol) was treated at 25 °C with a reagent prepared from $NbCl_5$ (2.0 mmol), Zn (3.0 mmol), and HMPA (4.0 mmol) in THF–benzene (1:2). [b] Isolated yields unless otherwise noted. [c] The Z/E ratios were determined by capillary GLPC and/or ^1H NMR analysis of the corresponding epoxides unless otherwise noted. [d] The reduction was conducted at 0 °C in DME–benzene (1:1); 4-fold excesses of low-valent niobium ($NbCl_5$ (4.0 mmol) and Zn (6.0 mmol)) were employed, as undesirable dimerization of the alkyne took place when unreacted alkyne remained. [e] GLPC yield. [f] The Z/E ratios were determined by capillary GLPC and/or ^1H NMR analysis of the product olefins. [g] Mixed solvent of THF–benzene–HMPA (1:2:1) was employed to accelerate the reduction. [h] The alkaline workup was conducted at −20 °C. [i] The Z/E ratio of the product after workup at 25 °C was 89/11. [j] The Z/E ratio of the product after workup at 25 °C was 93/7.

Table II. Reduction of Alkynes to (*Z*)-Alkenes by Means of a $TaCl_5$–Zn System[a]



run	R^1	R^2	t/h	yield/%[b]	Z/E[c]
1	n-$C_{10}H_{21}$	H	0.3	39	–
2	n-$C_{10}H_{21}$	H	1	52[d]	–
3	Ph	H	1	68[e]	–
4	n-C_5H_{11}	n-C_5H_{11}	0.5	85	>99/<1
5	$-(CH_2)_{10}-$		0.3	69	>99/<1[f]
6	Ph	n-C_6H_{13}	0.5	85	>99/<1[f]
7	c-C_6H_{11}	n-C_6H_{13}	4	80	>99/<1
8	t-Bu	n-C_7H_{15}	4.5	82[g]	>99/<1
9	Me_3Si	n-$C_{10}H_{21}$	2	79	89/11[f]
10	Bu	$CH_2{=}CH(CH_2)_3$	0.6	81[h]	>99/<1
11	n-$C_{10}H_{21}$	$CH_2{=}CH(CH_2)_4$	0.6	82[h]	>99/<1
12	n-$C_{10}H_{21}$	$HO(CH_2)_4$	0.5	80	>99/<1

[a] The alkyne (1.0 mmol) was treated at 25 °C with a reagent prepared from $TaCl_5$ (2.0 mmol) and Zn (3.0 mmol) in DME–benzene (1:1). [b] Isolated yields unless otherwise noted. [c] The Z/E ratios were determined by capillary GLPC and/or ^1H NMR analysis of the corresponding epoxides unless otherwise noted. [d] One equiv of $TaCl_5$ and 1.5 equiv of zinc were employed. Two equiv of TMEDA was added before addition of 1-dodecyne. Dodecane was produced in 2% yield. [e] GLPC yield. [f] The Z/E ratios were determined by capillary GLPC and/or ^1H NMR analysis of the product olefins. [g] Four equiv of $TaCl_5$ and 6 equiv of zinc were used, as the alkyne remained with the standard amounts of the reagent. [h] Internal alkene was produced in about 5% through overreduction of a terminal double bond.

aluminum in DME–benzene (1:1) before addition of alkyne was indispensable to get reproducible results.[11] Reduction of 1-dodecyne with the $NbCl_5$–Al system at 25 °C for 1.5 h afforded 1-dodecene in 89% yield, and quenching of the reaction mixture with NaOD–D_2O gave cis-dideuterated 1-dodecene (D: 100%). The reaction with a $NbCl_5$–magnesium system gave a complex mixture containing a small amount of the desired olefin.

Although heating was required to accomplish the complexation of alkynes with the low-valent niobium, the amount of $NbCl_5$ and zinc could be reduced to 1.0 and 1.5 equiv of the alkyne, respectively. For example, treatment of 6-dodecyne with 1.0 equiv of the $NbCl_5$ and 1.5 equiv of zinc at 25 °C for 24 h afforded (*Z*)-6-dodecene in 47% yield, along with unreacted 6-dodecyne in 27% yield.[12] Meanwhile, reaction of the same mixture at 90 °C for 6 h gave (*Z*)-6-dodecene in 81% yield. The latter 6-dodecene contains 87% of deuterium after workup with NaOD–D_2O. These observations suggest that a one-to-one complex[4b,13] of niobium and alkyne is produced as an intermediate.

Reduction of internal alkynes with the low-valent niobium gave (*Z*)-alkenes predominantly. In the case of internal alkynes having bulky substituents, partial isomerization took place during the hydrolysis which was suppressed appreciably by doing the hydrolysis at low temperature (−20 °C, runs 6–8). The rate of the formation of niobium–alkyne complexes depends upon the solvent system and the bulkiness of the substituents of alkynes. For example, in a mixed solvent of THF–benzene (1:2) and HMPA (double molar quantity of $NbCl_5$), 6-dodecene was produced in 74% yield by treatment with 2.0 equiv of $NbCl_5$ and 3.0 equiv of zinc for 20 h (run 3).[5,14] Alkynes **4** and **5** having bulky substituents such as *tert*-butyl and trialkylsilyl groups decreased in reactivity. Thus, the amount of HMPA was increased to 25 vol % of the mixed solvent of THF–benzene–HMPA in the case of alkynes **4** and **5**.

Terminal alkynes porimerized with the low-valent niobium in the THF–benzene–HMPA system. Reduction of 1-dodecyne was conducted in DME–benzene (1:1), and the desired 1-dodecene was obtained in 72% yield (run 1). Styrene was also produced in 81% yield from phenylacetylene (run 2). These results show sharp contrast to the $NbCl_5$–$NaAlH_4$ system,[2] where reduction of terminal alkynes gave a complex mixture.

Low-valent tantalum[15] can be produced from $TaCl_5$ and zinc by an analogous protocol to the niobium system. Complexation of alkynes with the $TaCl_5$–Zn system proceeded faster than those with the $NbCl_5$–Zn system; (*Z*)-alkenes are produced after hydrolysis (Table II). For example, the reduction of 6-dodecyne with $TaCl_5$–Zn system in DME and benzene (1:1) at 25 °C was finished within 0.5 h, while the same reduction with the $NbCl_5$–Zn system was not complete in 18 h.[12]

Isomerization to (*E*)-alkenes was suppressed except in the case of a silylalkyne (runs 7–9), when low-valent tan-

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(11) A mixture of $NbCl_5$ (4.0 equiv) and aluminum powder (6.0 equiv) in DME–benzene after ultrasonic irradiation shows a dark orange color.

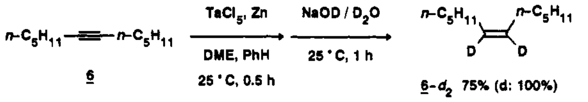
(12) Treatment of 6-dodecyne with 2 equiv of the $NbCl_5$–Zn reagent in DME–benzene (1:1) at 25 °C for 18 h gave 6-dodecene in 52% yield along with 18% of the starting alkyne. When 4 equiv of $NbCl_5$ was employed, the reduction of 6-dodecyne was completed in 5.5 h (80% yield).

(13) (a) Cotton, F. A.; Shang, M. *J. Am. Chem. Soc.* **1990**, *112*, 1584. (b) *Inorg. Chem.* **1990**, *29*, 2614. (c) *Ibid.* **1990**, *29*, 2619. (d) Cotton, F. A.; Feng, X. *Ibid.* **1990**, *29*, 3697. (e) Cotton, F. A.; Shang, M. *Organometallics* **1990**, *9*, 2131.

(14) When the reduction was conducted in a mixed solvent of THF–benzene–HMPA, introduction of deuteriums at vicinal olefinic positions of 6-dodecene with NaOD–D_2O was only 45%. Thus the mixed solvent of THF–benzene–HMPA was not employed in the following coupling reaction with phthaladehyde.[18a]

(15) Aldehydes and ketones were converted into the pinacol-type 1,2-diols with the low-valent tantalum (or niobium). For example, treatment of 3-phenylpropanal and cyclohexanone with the $TaCl_5$–Zn reagent in DME–benzene at 25 °C for 10 min afforded the corresponding 1,2-diols in 99% and 82% yields, respectively. Cinnamyl alcohol dimerized with loss of the hydroxyl group to afford a mixture of 1,5-dienes in 73% yield by the action of the low-valent tantalum. See also ref 2.

talum was employed. Quenching the reaction mixture of the reduction of 6-dodecyne with the low-valent tantalum by the addition of NaOD–D_2O gave also a vicinal dideuterated olefin **6-d_2** in 75% yield (eq 3). Terminal alkynes are too reactive with the $TaCl_5$–Zn reagent, and the yield with the tantalum reagent was lower than that with the niobium reagent (run 1). Best yield was obtained when 2.0 equiv of TMEDA was added before addition of 1-dodecyne (run 2).



(3)

Olefinic double bonds which were capable of participating in a cyclization remained intact (runs 10 and 11). This observation shows a sharp contrast to the reaction with low-valent zirconium.[16] Reduction of an alkyne having a hydroxyl group was performed in excellent yield (run 12).

Low-valent group 5 metals react with alkynes to form metal–alkyne complexes.[4,7,17,18] Since low-valent group 5 metal complexes are reported to catalyze cyclotrimerization of acetylenes,[4a,10] it is of considerable interest that no benzene derivative was observed throughout the reaction in DME–benzene (1:1). Introduction of deuterium at a cis-vicinal position of alkenes suggests that the niobium– and tantalum–alkyne complexes reported here are capable to use as a cis vicinal dianion reagent.[18]

Experimental Section

General. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Benzene, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone just before use. Hexamethylphosphoric triamide (HMPA) was distilled from calcium hydride and stored over 4A molecular sieves. Zinc dust purchased from Wako Pure Chemical Industries, Ltd. (GR grade), was activated by washing several times with 5% hydrochloric acid, washing in turn with water, methanol, and ether, and drying in vacuo according to Fieser and Fieser.[19] Internal alkynes were prepared according to the standard procedure described in refs 20–23. Distillation of small amounts of products was performed with a Büchi Kugelrohr, and boiling points are indicated by an air-bath temperature without correction. IR spectra were determined with a JASCO IR-810 spectrometer. Mass spectra were obtained with a Hitachi M-80 mass spectrometer. ^1H and ^{13}C NMR spectra were determined with a Varian XL-200 spectrometer. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane using the δ scale. Column chromatography was done with silica gel (200 mesh). GLPC was performed with a Hitachi 163 gas chromatograph using a Silicone OV-1 capillary column. Elemental analyses were performed by the staff at the Elemental Analyses Center of Kyoto University.

Reduction of 1-Dodecyne with a $NbCl_5$–Zn System. In a 50-mL reaction flask was placed $NbCl_5$ (1.1 g, 4.0 mmol) under an argon atmosphere. To the salt were added at 25 °C benzene (5 mL) and DME (5 mL) successively. Zinc dust (0.39 g, 6.0 mmol) was added to the stirring pale orange solution of $NbCl_5$, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned dark brown with slightly exothermic process. To the mixture was added at 0 °C a solution of 1-dodecyne (0.17 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 0 °C for 1 h. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The precipitated white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3 × 5 mL). The combined filtrate and washings were dried over $MgSO_4$ and concentrated in vacuo. Purification by column chromatography on silica gel with hexane as eluent gave 0.12 g (72%) of 1-dodecene.

Typical Procedure for Partial Reduction of an Internal Alkyne with a $NbCl_5$–Zn System. Procedure A. To a stirred solution of $NbCl_5$ (1.1 g, 4.0 mmol) in DME and benzene (1:1, 10 mL) was added zinc (0.39 g, 6.0 mmol) under an argon atmosphere, and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 6-dodecyne (0.17 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C for 5.5 h. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The precipitated white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3 × 5 mL). The filtrate and washings were dried over $MgSO_4$ and concentrated in vacuo. Purification by column chromatography on silica gel with hexane as eluent gave 0.13 g (80%) of 6-dodecene. **(b) Procedure B.** To a stirred pale orange solution of $NbCl_5$ (0.54 g, 2.0 mmol) in THF and benzene (1:2, 15 mL) were added HMPA (0.70 mL, 4.0 mmol) and zinc (0.20 g, 3.0 mmol) successively under an argon atmosphere, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned from purple to dark blue with slightly exothermic process. To the mixture was added at 25 °C a solution of 6-dodecyne (0.17 g, 1.0 mmol) in THF and benzene (1:2, 1.5 mL), and the resulting mixture was stirred at 25 °C for 20 h. Aqueous alkaline workup similar to procedure A followed by filtration, concentration, and purification by column chromatography gave 0.12 g (74%) of 6-dodecene. **(c) Procedure C.** To a stirred pale orange solution of $NbCl_5$ (0.54 g, 2.0 mmol) in a mixed solvent of THF, benzene, and HMPA (1:2:1, 20 mL) was added zinc (0.20 g, 3.0 mmol) under an argon atmosphere, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned from wine red to dark purple. To the mixture was added at 25 °C a solution of 1-phenyl-1-octyne (0.19 g, 1.0 mmol) in THF and benzene (1:2, 1.5 mL), and the resulting mixture was stirred at 25 °C for 20 h. Aqueous alkaline workup similar to procedure A followed by filtration, concentration, and purification by column chromatography gave 0.16 g (86%) of 1-phenyl-1-octyne.

Typical Procedure for Partial Reduction of an Internal Alkyne with a $TaCl_5$–Zn System. To a stirred solution of $TaCl_5$ (0.72 g, 2.0 mmol) in DME and benzene (1:1, 10 mL) was added zinc (0.20 g, 3.0 mmol) at 25 °C under an argon atmosphere, and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 6-docecyne (0.17 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the resulting mixture was stirred at 25 °C for 30 min. Aqueous NaOH solution (15%, 2 mL) was added, and the whole mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3 × 5 mL). The crude product was dried over $MgSO_4$ and concentrated in vacuo. Purification by column chromatography on silica gel with hexane as eluent gave 0.14 g (85%) of 6-dodecene.

(*Z*)-1-Cyclohexyl-1-octene. Bp: 62–63 °C (bath temperature, 1 Torr). IR (neat): 2922, 2848, 1730, 1449, 1379, 1269, 889 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.89 (t, $J = 6.5$ Hz, 3 H), 1.0–1.2 (m, 2 H), 1.1–1.5 (m, 12 H), 1.5–1.9 (m, 4 H), 1.9–2.2 (m, 2 H), 2.2–2.4 (m, 1 H), 5.1–5.4 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 26.1, 26.2, 27.5, 29.0, 30.0, 31.8, 33.4, 36.3, 128.1, 136.0. MS: m/z (rel intensity) 194 (M^+, 5), 109 (65), 96 (100), 82 (29), 67 (17), 55 (34). Anal. Calcd for $C_{14}H_{26}$: C, 86.52; H, 13.48. Found: C, 86.46; H, 13.57. The E/Z ratio was determined by ^1H NMR analysis of

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the corresponding epoxide.[24] ***cis*-1-Cyclohexyl-1,2-epoxyoctane.** ^{1}H NMR (CDCl$_3$): δ 0.81 (t, J = 6.9 Hz, 3 H), 0.9–1.5 (m, 12 H), 1.3–1.6 (m, 4 H), 1.4–1.8 (m, 4 H), 1.8–2.0 (m, 1 H), 2.55 (dd, J = 4.0, 8.0 Hz, 1 H), 2.8–2.9 (m, 1 H).

(*Z*)-2,2-Dimethyl-3-undecene. Bp: 88–90 °C (bath temperature, 13 Torr). IR (neat): 2954, 2922, 1729, 1466, 1363, 1273 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.88 (t, J = 6.7 Hz, 3 H), 1.08 (s, 9 H), 1.1–1.5 (m, 10 H), 2.0–2.3 (m, 2 H), 5.15 (dt, J = 12.0, 7.0 Hz, 1 H), 5.31 (d, J = 12.0 Hz, 1 H). ^{13}C NMR (CDCl$_3$): δ 14.1, 22.7, 28.4, 29.3, 29.4, 30.4, 31.2, 31.9, 33.1, 129.1, 139.6. MS: m/z (rel intensity) 182 (M$^+$, 3), 139 (3), 97 (20), 83 (100), 69 (69), 55 (48). Anal. Calcd for $C_{13}H_{26}$: C, 85.63, H, 14.37. Found: C, 85.61; H, 14.54. The E/Z ratio was determined by ^{1}H NMR analysis of the corresponding epoxide.[24] ***cis*-2,2-Dimethyl-3,4-epoxyundecane.** ^{1}H NMR (CDCl$_3$): δ 0.87 (t, J = 6.8 Hz, 3 H), 0.98 (s, 9 H), 1.2–1.5 (m, 10 H), 1.6–1.9 (m, 2 H), 2.63 (d, J = 4.2 Hz, 1 H), 2.8–2.9 (m, 1 H). **(*E*)-2,2-Dimethyl-3-undecene.** ^{1}H NMR (CDCl$_3$): δ 0.92 (t, J = 6.7 Hz, 3 H), 0.99 (s, 9 H), 1.2–1.5 (m, 10 H), 1.9–2.1 (m, 2 H), 5.29 (dt, J = 15.7, 6.3 Hz, 1 H), 5.43 (d, J = 15.7 Hz, 1 H). ***trans*-2,2-Dimethyl-3,4-epoxyundecane.** ^{1}H NMR (CDCl$_3$): δ 0.81 (t, J = 6.8 Hz, 3 H), 0.85 (s, 9 H), 1.1–1.5 (m, 10 H), 1.5–1.6 (m, 2 H), 2.45 (d, J = 2.3 Hz, 1 H), 2.7–2.8 (m, 1 H).

(*Z*)-1-(Trimethylsilyl)-1-dodecene. Bp: 76–78 °C (bath temperature, 1 Torr). IR (neat): 2922, 2852, 1607, 1466, 1248, 837, 761, 688 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.08 (s, 9 H), 0.93 (t, J = 6.8 Hz, 3 H), 1.1–1.5 (m, 16 H), 2.0–2.2 (m, 2 H), 5.45 (d, J = 14.0 Hz, 1 H), 6.29 (dt, J = 14.0, 7.3 Hz, 1 H). ^{13}C NMR (CDCl$_3$): δ 0.58, 14.1, 22.7, 29.4, 29.8, 32.0, 33.6, 128.7, 149.3. MS: m/z (rel intensity) 240 (M$^+$, 0.8), 225 (50), 114 (27), 73 (100), 59 (61). Anal. Calcd for $C_{15}H_{32}Si$: C, 74.91; H, 13.41. Found: C, 74.48; H, 13.57. The E/Z ratio was determined by ^{1}H NMR analysis. **(*E*)-1-(Trimethylsilyl)-1-dodecene.** ^{1}H NMR (CDCl$_3$): δ 0.02 (s, 9 H), 0.85 (t, J = 6.7 Hz, 3 H), 1.1–1.5 (m, 16 H), 2.0–2.2 (m, 2 H), 5.59 (d, J = 18.0 Hz, 1 H), 6.02 (dt, J = 18.0, 6.1 Hz, 1 H).

(*Z*)-1,6-Undecadiene.[25] ^{1}H NMR (CDCl$_3$): δ 0.90 (t, J = 7.0 Hz, 3 H), 1.2–1.4 (m, 4 H), 1.46 (dd, J = 6.9, 7.3 Hz, 2 H), 1.9–2.2 (m, 6 H), 4.95 (d, J = 10.3 Hz, 1 H), 5.01 (d, J = 17.0 Hz, 1 H), 5.3–5.5 (m, 2 H), 5.82 (ddt, J = 10.3, 17.0, 6.8 Hz, 1 H). The E/Z ratio was determined by ^{1}H NMR analysis of the corresponding epoxide.[24] ***cis*-6,7-Epoxy-1-undecene.** ^{1}H NMR (CDCl$_3$): δ 0.93 (t, J = 6.8 Hz, 3 H), 1.2–1.8 (m, 10 H), 2.0–2.3 (m, 2 H), 2.9–3.0 (m, 2 H), 4.98 (d, J = 17.1 Hz, 1 H), 5.01 (d, J = 10.3 Hz, 1 H), 5.82 (ddt, J = 10.3, 17.1, 6.6 Hz, 1 H).

(*Z*)-1,7-Octadecadiene. Bp: 103–105 °C (bath temperature, 0.20 Torr). IR (neat): 2922, 2852, 1735, 1642, 1460, 1271, 991 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.88 (t, J = 6.9 Hz, 3 H), 1.2–1.5 (m, 16 H), 1.3–1.5 (m, 4 H), 1.9–2.2 (m, 6 H), 4.95 (d, J = 10.3 Hz, 1 H), 5.00 (d, J = 16.9 Hz, 1 H), 5.3–5.5 (m, 2 H), 5.82 (ddt, J = 10.3, 16.9, 6.6 Hz, 1 H). ^{13}C NMR (CDCl$_3$): δ 14.1, 22.7, 27.0, 27.2, 28.6, 29.2, 29.4, 29.6, 29.7, 29.8, 31.9, 33.7, 114.2, 129.6, 130.1, 139.0. MS: m/z (rel intensity) 250 (M$^+$, 4), 123 (9), 96 (75), 82 (100), 67 (76), 55 (79). Anal. Calcd for $C_{18}H_{34}$: C, 86.32; H, 13.68. Found: C, 86.18; H, 13.61. The E/Z ratio was determined by ^{1}H NMR analysis of the corresponding epoxide.[24] ***cis*-7,8-Epoxy-1-octadecene.** ^{1}H NMR (CDCl$_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.2–1.5 (m, 14 H), 1.3–1.6 (m, 10 H), 2.0–2.1 (m, 2 H), 2.9–3.0 (m, 2 H), 4.95 (d, J = 10.2 Hz, 1 H), 5.01 (d, J = 17.1 Hz, 1 H), 5.81 (ddt, J = 10.2, 17.1, 6.6 Hz, 1 H).

(*Z*)-5-Octadecen-1-ol. Bp: 146–147 °C (bath temperature, 0.30 Torr). IR (neat): 3318, 2922, 2850, 1652, 1466, 1067 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.1–1.5 (m, 21 H), 1.4–1.5 (m, 2 H), 1.5–1.7 (m, 2 H), 1.9–2.2 (m, 4 H), 3.6–3.7 (m, 2 H), 5.3–5.5 (m, 2 H). ^{13}C NMR (CDCl$_3$): δ 14.2, 22.7, 25.9, 26.9, 27.3, 29.4, 29.6, 29.7, 31.9, 32.4, 62.9, 129.3, 130.4. MS: m/z (rel intensity) 250 (M$^+$ − H_2O, 6), 123 (10) 96 (58), 82 (100), 41 (66). Anal. Calcd for $C_{18}H_{36}O$: C, 80.53; H, 13.52. Found: C, 80.56; H, 13.63. The E/Z ratio was determined by ^{1}H NMR analysis of the epoxide[24] of the *tert*-butyldimethylsilyl ether of the alcohol. ***cis*-5,6-Epoxy-1-(*tert*-butyldimethylsiloxy)octadecane.** ^{1}H NMR (CDCl$_3$): δ 0.03 (s, 6 H), 0.86 (s, 12 H), 1.2–1.4 (m, 16 H), 1.4–1.8 (m, 12 H), 2.9–3.0 (m, 2 H), 3.62 (t, J = 5.9 Hz, 2 H).

Registry No. **1**, 765-03-7; **2**-d_2, 127863-12-1; **3a**, 87969-78-6; **3b**, 138384-24-4; **4**, 125641-95-4; **5**, 121134-52-9; **6**, 6975-99-1; **6**-d_2, 125642-23-1; phenylacetylene, 536-74-3; cyclodecyne, 3022-41-1; 1-phenyl-1-octyne, 16967-02-5; 1-cyclohexyl-1-octyne, 125641-94-3; (*Z*)-6-dodecene, 7206-29-3; (*Z*)-cyclododecene, 1129-89-1; (*Z*)-1-phenyl-1-octene, 42036-72-6; (*Z*)-1-cyclohexyl-1-octene, 62444-54-6; *cis*-1-cyclohexyl-1,2-epoxyoctane, 106262-67-3; *cis*-2,2-dimethyl-3,4-epoxyundecane, 138813-13-5; *trans*-2,2-dimethyl-3,4-epoxyundecane, 138813-14-6; (*Z*)-2,2-dimethyl-3-undecene, 125642-19-5; (*Z*)-1-(trimethylsilyl)-1-dodecene, 70875-30-8; (*E*)-1-cyclohexyl-1-octene, 87393-89-3; (*E*)-2,2-dimethyl-3-undecene, 14033-68-2; (*E*)-1-(trimethylsilyl)-1-dodecene, 70875-31-9; (*Z*)-1,6-undecadiene, 91914-03-3; *cis*-6,7-epoxy-1-undecane, 138813-17-9; (*Z*)-1,7-octadecadiene, 127863-11-0; *cis*-7,8-epoxy-1-octadecene, 138813-15-7; (*Z*)-5-octadecen-1-ol, 41207-39-0; *cis*-5,6-epoxy-1-(*tert*-butyldimethylsiloxy)octadecane, 138813-16-8; 1-undecen-6-yne, 127863-09-6; 1-octadecen-7-yne, 127863-10-9; 5-hexadecyn-1-ol, 72443-47-1; (*Z*)-5-hexadecen-1-ol, 106463-48-3; niobium chloride, 10026-12-7; zinc, 7440-66-6; tantalum chloride, 7721-01-9; 1-dodecene, 112-41-4; styrene, 100-42-5.

Supplementary Material Available: Spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, MS) for internal alkynes and two experimental procedures (5 pages). Ordering information is given on any current masthead page.

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[24] Epoxidation was conducted with mCPBA in CH_2Cl_2 at 0 °C. The following procedure was modified. Paquette, L. A.; Barrett, J. H. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. V, p 467.

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High Regioselectivity in the Alternative, Reductive Cleavages of Terminal Epoxides with Aluminum Reagents[1]

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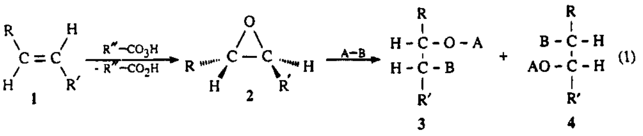
Introduction

One of the potentially most versatile methods for functionalizing a carbon skeleton is the Prilezhaev epoxidation of a carbon–carbon double bond (**1**)[2] and the ring opening of the oxirane **2** by a polar reagent, A–B (eq 1):[3]



With an unsymmetrical alkene, even if the ring opening were to occur in a stereospecific, S$_N$2 manner (e.g., **3** and **4**), there remains the further complication of a nonregioselective ring opening leading to various proportions of regioisomers **3** and **4**. A significant improvement in the utility and versatility of this method for organic synthesis would be the discovery of A–B reagents and experimental conditions that cleave oxiranes in a highly regioselective manner and thereby lead either to product **3** or to product **4** in high yield.

For this study, we have chosen oxiranes derived from terminal olefins as our test substrates because functionality at or near the end of a carbon chain is often the most valuable site for carbon–carbon chain elongation. As a potentially valuable cleavage process, we have selected reduction with sources of aluminum hydride.

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