of sodium thiosulfate (25 mL) and water (2 × 25 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded a crude product, which was purified by distillation to provide 1-phenyl-(*E*)-1-hexene (**11a**; 1.18 g, 74%), bp 84.86 °C (2 mm), n^{20}_D 1.5280. GC analysis showed >99% stereochemical purity. IR (neat): ν 1645, 1594, 964, 740, and 690 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 0.80–1.03 (distorted t, 3 H), 1.16–1.53 (m, 4 H), 2.00–2.33 (m, 2 H), 5.83–6.10 (m, 2 H), and 7.03–7.26 (m, 5 H).

2-Methyl-(*E*)-3-octene. IR (neat): ν 1655 and 967 cm^{-1} (C=C). ^1H NMR ($CDCl_3$/TMS): δ 0.83–1.03 (m, 9 H), 1.16–1.53 (m, 4 H), 1.83–2.46 (m, 3 H), and 5.26–5.46 (m, 2 H).

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Pheromones via Organoboranes. 3. Vinylic Organoboranes. 10. Stereospecific Synthesis of (*Z*)- and (*E*)-6- and -7-Alken-1-ols via Boracyclanes[1]

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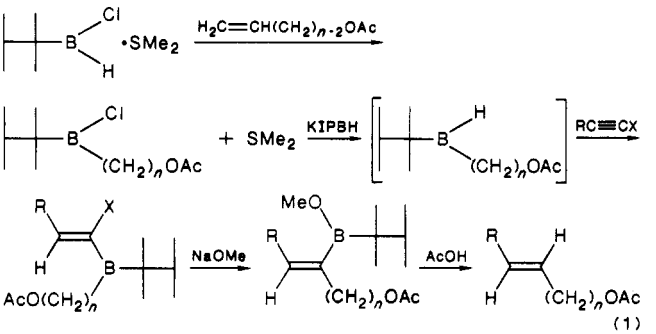
Treatment of *B*-(*E*)-1-alkenylborinanes, obtained via monohydroboration of 1-alkynes with borinane, with iodine in the presence of a base results in the migration of one end of the cycloalkyl chain from boron to the adjacent carbon, producing intermediates containing the seven-membered borepane moiety, which undergo rapid deiodoboronation to afford the (*Z*)-6-alkenyl-1-boronate esters. These boronate esters, upon oxidation, provide (*Z*)-6-alken-1-ols. The procedure is successfully extended to *B*-(*E*)-1-alkenylborepane derivatives to produce (*Z*)-7-alken-1-ols. The preparation of (*E*)-6- and -7-alken-1-ols has been carried out via borinane and borepane derivatives. Borinane, as prepared previously, hydroborates cleanly 1-bromo-1-alkynes to provide the *B*-((*Z*)-1-bromo-1-alkenyl)borinanes. Treatment of these boron intermediates with sodium methoxide results in the displacement of bromine by one end of the boracycloalkyl moiety, producing the corresponding vinylboranes containing the seven-membered borepane moiety. The intermediates, upon controlled protonolysis, followed by oxidation, afford the (*E*)-6-alken-1-ols. The methodology was extended to borepane derivatives to provide (*E*)-7-alken-1-ols. The above procedures constitute a simple, very convenient, stereospecific, and general one-pot synthesis of (*Z*)- and (*E*)-6- and -7-alken-1-ols. The methodology has been applied to the synthesis of representative pheromones containing a (*Z*)- or an (*E*)-alkene moiety in good yields.

Organoboranes play an important role in bringing latitude to organic synthesis.[3] Highly stereospecific syntheses of (*Z*)- and (*E*)-disubstituted alkenes via organoboranes are well documented in the literature.[4,5] Recently we reported applications of the general stereospecific synthesis of (*E*)-disubstituted olefins via thexylchloroborane–dimethyl sulfide to the synthesis of pheromones containing an (*E*)-alkene moiety[6] (eq 1).



(1)

The synthesis[7] of unsaturated alcohols has attracted considerable attention from organic chemists in recent years because such alcohols[8,9] or acetates[8,10] are known to be insect pheromones. For example, (*Z*)-7-dodecen-1-ol (**2a**) is the pheromone of the male moths of lepidoptera, *Raphia frater Grt* (Noctuidae),[9] and (*Z*)-7-dodecen-1-yl

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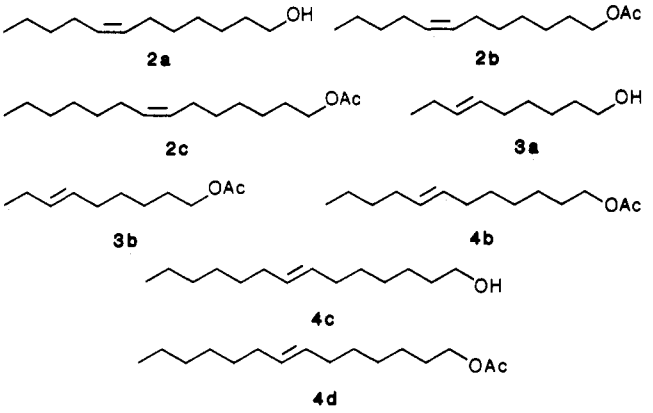
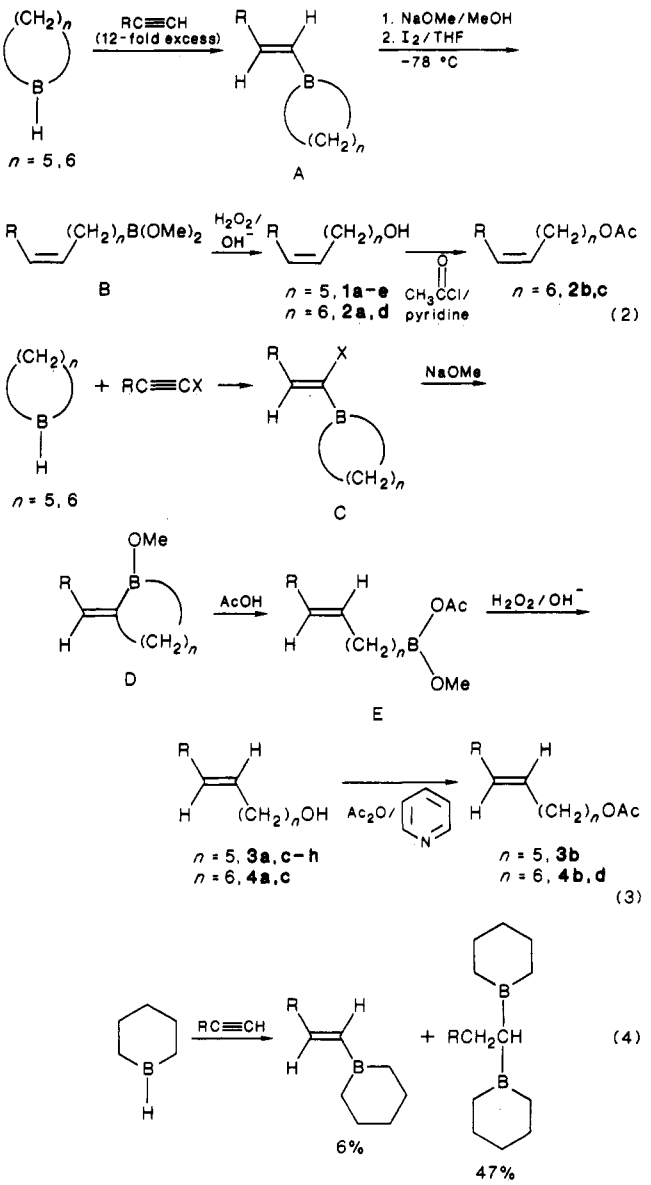
acetate (**2b**) is the sex attractant of soybean loopers, *Pseudoplusia includens* (Walker),[11] and also of the cabbage looper, *Trichoplusia ni* (Hubner).[12] (*Z*)-7-Tetradecen-1-yl acetate (**2c**) is the pheromone of the *Amathes c-nigrum* found both in Japan[13] and in Germany.[14] (*E*)-6-Nonen-1-ol (**3a**) is the sex pheromone produced by the males of the Mediterranean fruitfly, *Ceratitis capitata*,[15] and its corresponding acetate (**3b**) is the attractant for the female melonfly, *Dacus cucurbitae*.[16,17] (*E*)-7-Dodecen-1-ol acetate (**4b**) is the sex pheromone of the moth, *Argyroploce leucotreta M*,[18] and (*E*)-7-tetradecen-1-ol (**4c**) and the corresponding acetate (**4d**) are sex pheromones of the corn earworm, *Heliothis zea* (Boddie).[19]



Since the presence of minor isomers frequently inhibits the biological activity of such sex attractants,[20] a highly stereospecific synthesis of these classes of compounds is desirable. Many reactions of organoboranes are highly stereospecific.[21] Therefore, it appeared that procedures based on organoborane chemistry should be especially favorable for such syntheses. We herein report a highly stereospecific synthesis of both (*Z*)- and (*E*)-6- and -7-alken-1-ols, providing a convenient route to the synthesis of pheromones **2**–**4** via organoboranes (eq 2 and 3).

Results and Discussion

Synthesis of (*Z*)-6- and -7-Alken-1-ols. Borinane was prepared as described in the literature.[22] The hydroboration of 1-alkynes with 1 equiv of borinane in tetrahydrofuran gave *B*-(*E*)-1-alkenylborinanes along with dihydroborated product[23] (eq 4). We achieved clean monohydroboration by using a large excess of 1-alkyne (12-fold excess). However, the excess alkyne can be recovered quantitatively by distillation from the hydroborated product.



Iodination of the *B*-(*E*)-1-alkenylborinane (A) thus obtained in the presence of sodium methoxide resulted in the migration of one end of the cycloalkyl chain from the boron to the adjacent carbon, producing an intermediate containing the seven-membered borepane moiety, which underwent a rapid deiodoboronation to afford (*Z*)-6-alkenylboronate esters (B). These boronate esters were oxidized with alkaline hydrogen peroxide to provide (*Z*)-6-alken-1-ols in good yields. Representative (*Z*)-6-alken-1-ols (**1a–e**) were prepared by the reaction sequence shown in eq 2, and the results are summarized in Table I. The present methodology was extended to *B*-(*E*)-1-alkenylborepane derivatives to produce (*Z*)-7-alken-1-ols. Unfortunately, we encountered one difficulty. The monohydroboration of 1-alkynes with borepane, obtained via the hydridation[24] of *B*-chloroborepane,[25] is also accompanied by a competing dihydroboration (eq 5). This difficulty could also be surmounted by excess of 1-alkyne

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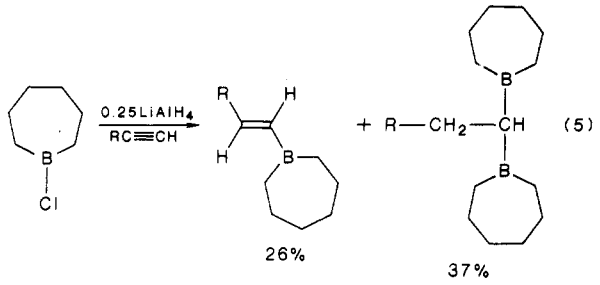

(12-fold excess), thus providing a clean monohydroboration product. Consequently, this reaction sequence was employed for the synthesis of representative insect pheromones belonging to the class of (*Z*)-7-alken-1-ols. Thus, **2a** and **2d** were prepared in high yields and in excellent stereochemical purities and were converted to the corresponding acetates, **2b** and **2c**, respectively (Table II).

Synthesis of (*E*)-6- and -7-Alken-1-ols. Hydroboration of 1-halo-1-alkyne with borinane provided the corresponding *B*-(*Z*)-(1-halo-1-alkenyl)borinane (C).[26] This was then treated with sodium methoxide in methanol to obtain the borepane intermediate (D). Controlled protonolysis of the borepane intermediate with acetic acid afforded the boronate ester (E), which, upon the usual oxidation by alkaline hydrogen peroxide, gave the (*E*)-6-alken-1-ols in high yields (eq 3). Consequently, (*E*)-6-nonen-1-ol (**3a**), a pheromone, was prepared in 80% yield and converted into the corresponding acetate (**3b**), the natural sex attractant, in 90% yield. Our results are summarized in Table III. Application of the present procedure to borepane derivatives afforded (*E*)-7-alken-1-ols (eq 3), and the results are summarized in Table IV.

It was previously established that, in the base-induced rearrangement of 1-bromo-1-alkenyldialkylboranes, the migrating group from boron becomes trans to the alkyl group of the original alkyne. Thus the 6- and 7-alken-1-ols synthesized, as in eq 3, should possess trans stereochemistry. Trans stereochemistry was confirmed by a strong IR absorption at ν = ~967 cm^{-1} in each product.[27] Furthermore, no *Z* isomer could be detected by GC on a glass capillary gas chromatograph, although it was established that the Z and E isomers are readily separated on this instrument.

Conclusions

In summation, we have successfully utilized the readily available borinane and borepane for the stereospecific synthesis of (*Z*)- and (*E*)-6- and -7-alken-1-ols. These procedures represent a very convenient, general, one-pot, and stereospecific synthesis of (*Z*)- and (*E*)-6- and -7-alken-1-ols, providing a simple route to the synthesis of pheromones. The success realized with both borinane and borepane suggests that this procedure is probably general for the boracyclanes. It only required the development of practical procedures for the synthesis of such boracyclanes to make this a procedure of wide generality. We are exploring such procedures for the synthesis of boracyclanes.

Experimental Section

General Procedures. All boiling points are uncorrected. All glassware was predried at 140 °C for several hours, assembled hot, and cooled under a stream of nitrogen. Syringes were assembled and fitted with needles while hot and then cooled. GC analyses were carried out either on a Varian 1400 gas chromatograph (column 12 ft × $^1/_8$ in. packed with 10% SE-30 on Chromosorb W AW DMCS) or on a Hewlett-Packard 5730A gas chromatograph equipped with an FID detector. GC analyses were carried out on a Carbowax 20M column (50 m in length), and isothermal analyses were conducted at 130 °C. Analyses of some compounds were carried out on a 5890A capillary gas chromatograph. IR spectra were recorded on a Perkin-Elmer 1420 ratio-recording infrared spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Perkin-Elmer R-32 and FT-80A spectrometers, respectively. ^{1}H NMR spectra of some compounds were taken on a Varian T-60 spectrometer. All reactions were carried out under a static pressure of nitrogen in flasks fitted with septum-covered sidearms by standard techniques for handling air-sensitive materials.[3]

Materials. Borinane[22] and *B*-chloroborepane[25] were prepared according to literature procedure. The alkynes were purchased from Farchan Laboratories. Tetrahydrofuran was freshly distilled from benzophenone ketyl solution. The 1-halo-1-alkynes were prepared by the action of bromine or iodine on the corresponding alkynyllithium.[28]

Preparation of (*Z*)-6-Undecen-1-ol (1a) is representative. In a dry, 250-mL flask equipped with a magnetic stirring bar and septum inlet were placed 1-hexyne (120 mmol, 13.80 mL) and 20 mL of tetrahydrofuran. The flask was cooled to −78 °C, and borinane in tetrahydrofuran (10 mmol, 5.30 mL of 1.90 M solution) was slowly added. The reaction mixture was stirred at −78 °C for 1 h and then at 0 °C for 2 h. Then tetrahydrofuran and excess of 1-hexyne were distilled off under reduced pressure. The resulting vinylborane was dissolved in tetrahydrofuran (20 mL), and the solution was cooled to −78 °C. To this solution at −78 °C was added sodium methoxide in methanol (20 mmol, 4.46 mL of 4.49 M solution), followed by the addition of iodine (10 mmol, 2.54 g) in tetrahydrofuran (10 mL). After 3 h, any excess iodine was decolorized by adding an aqueous solution of sodium thiosulfate, and the reaction mixture was allowed to warm to room temperature. The reaction mixture was oxidized in the usual way to provide, after distillation, (*Z*)-6-undecen-1-ol (**1a**; 1.10 g, 65%), bp 78–80 °C (0.01 mm), n^{20}_D 1.4613, GC purity >99%. IR (neat): ν 3332 (—OH), 1651, 870 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 0.93 (distorted t, 3 H), 1.20–1.73 (m, 10 H), 1.83–2.26 (m, 4 H), 2.43 (s, 1 H, exchangeable with D_2O), 3.60 (distorted t, 2 H), and 5.20–5.43 (m, 2 H). Mass spectrum: *m/e* (M^+) 170.

(*Z*)-6-Decen-1-ol (1b). Following the above procedure, (*Z*)-6-decen-1-ol was prepared in 63% yield. IR (neat): ν 3332 (—OH), 1648, 876 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 0.93 (distorted t, 3 H), 1.66 (m, 4 H), 3.06 (s, 1 H, exchangeable with D_2O), 3.60 (distorted t, 2 H), and 5.26–5.46 (m, 2 H). Mass spectrum: *m/e* (M^+) 156.

8-Methyl-(*Z*)-6-nonen-1-ol (1c). IR (neat): ν 3345 (—OH), 1651, 878 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 0.93 (d, J = 6 Hz, 6 H), 1.13–1.63 (m, 6 H), 1.93–2.16 (m, 3 H), 2.76 (s, 1 H, exchangeable with D_2O), 3.60 (distorted t, 2 H), and 5.10–5.26 (m, 2 H). Mass spectrum: *m/e* (M^+) 156.

7-Cyclohexyl-(*Z*)-6-hepten-1-ol (1d). IR (neat): ν 3332 (—OH), 1651, 841 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 1.03–2.13 (m, 13 H), 2.80 (s, 1 H, exchangeable with D_2O), 3.60 (distorted t, 2 H), and 4.96–5.33 (m, 2 H). Mass spectrum: *m/e* (M^+) 192.

8,8-Dimethyl-(*Z*)-6-nonen-1-ol (1e). IR (neat): ν 3332 (—OH), 1648, 877 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 1.10 (s, 9 H), 1.33–1.53 (m, 6 H), 2.10–2.26 (m, 2 H), 2.83 (s, 1 H, exchangeable with D_2O), 3.60 (distorted t, 2 H), and 5.06–5.30 (m, 2 H). Mass spectrum: *m/e* (M^+) 170.

Preparation of (*Z*)-7-Dodecen-1-ol (2a) is representative. In a dry, 250-mL flask containing 3.90 g (30 mmol) of *B*-chloroborepane were placed tetrahydrofuran (20 mL) and 1-hexyne (360 mmol, 41.40 mL) at −78 °C. To this cooled mixture was added slowly lithium aluminum hydride in tetrahydrofuran (7.5 mmol) with vigorous stirring. After the addition, the reaction mixture was allowed to warm to 0 °C, and stirring was continued for 2 h at 0 °C. Then, tetrahydrofuran and excess of 1-hexyne were distilled off under reduced pressure. The resulting vinylborane was dissolved in tetrahydrofuran (40 mL), and the solution was cooled to −78 °C. To this solution at −78 °C was added a solution of sodium methoxide in methanol (120 mmol, 26.60 mL of a 4.50

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Table I. Stereospecific Synthesis of (*Z*)-6-Alken-1-ols via Borinane[a]

1-alkyne	product[b]	yield,[c] %	bp, °C (mm)	n^{20}_D
1-hexyne	(*Z*)-6-undecen-1-ol (**1a**)	65	78–80 (0.01)	1.4613
1-pentyne	(*Z*)-6-decen-1-ol (**1b**)	63	74–76 (0.30)	1.4567
3-methyl-1-butyne	8-methyl-(*Z*)-6-nonen-1-ol (**1c**)	62	62–64 (0.10)	1.4630
cyclohexylethyne	7-cyclohexyl-(*Z*)-6-hepten-1-ol (**1d**)	68	106–108 (0.25)	1.4805
3,3-dimethyl-1-butyne	8,8-dimethyl-(*Z*)-6-nonen-1-ol (**1e**)	75	65–67 (0.01)	1.4524

[a] All reactions were carried out on a 10-mmol scale. [b] Stereochemical purities of all products are >98% by capillary GC analysis. [c] Yields of pure products isolated by distillation based on borinane.

Table II. Stereospecific Synthesis of (*Z*)-7-Alken-1-ols and Their Acetates from 1-Alkyne and Borepane[a]

1-alkyne	product[b,c]	yield, %	bp, °C (mm)	n^{20}_D
1-hexyne	(*Z*)-7-dodecen-1-ol (**2a**)	78[d]	115–117 (0.90), [lit.[29] 74–76 (0.01)]	1.4549
	1-acetoxy-(*Z*)-7-dodecene (**2b**)	92[e]	80–81 (0.01) [lit.[7a] 85–90 (0.08)]	1.4432 [lit.[7a] n^{25}_D 1.4420]
1-octyne	(*Z*)-7-tetradecen-1-ol (**2c**)	80[d]	110–112 (0.02) [lit.[29] 94–96 (0.01)]	1.4566
	1-acetoxy-(*Z*)-7-tetradecene (**2d**)	93[e]	105–107 (0.01) [lit.[29] 102–104 (0.01)]	1.4465 [lit.[31] n^{24}_D 1.4463]

[a] All reactions were carried out on a 30-mmol scale. [b] Chemical purities of all products are >97% by GC analysis on a 6-ft SE-30 column. [c] Isomeric purities are ≃99% by ^{13}C NMR[32] analysis. [d] Yields of pure products isolated by distillation, based on borepane. [e] Isolated yields from the corresponding alcohols.

Table III. Stereospecific Synthesis of (*E*)-6-Alken-1-ols from 1-Halo-1-alkynes and Borinane[a]

1-halo-1-alkyne	product[b]	yield,[c] %	bp, °C (mm)	n^{20}_D
1-iodo-1-butyne	(*E*)-6-nonen-1-ol (**3a**)	80	84–85 (3.00), [lit.[30] 70–71 (0.05)]	1.4485
	1-acetoxy-(*E*)-6-nonene (**3b**)	90[d]	89–90 (3.00), [lit.[30] 65–70 (0.30)]	1.4352
1-bromo-1-pentyne	(*E*)-6-decen-1-ol (**3c**)	78	78–79 (0.8), [lit.[30] 72 (0.03)]	1.4479
1-bromo-1-hexyne	(*E*)-6-undecen-1-ol (**3d**)	81	84–85 (0.60), [lit.[30] 83–84 (0.03)]	1.4482
1-bromo-1-heptyne	(*E*)-6-dodecen-1-ol (**3e**)	76	98–99 (0.70)	1.4514
1-bromo-1-octyne	(*E*)-6-tridecen-1-ol (**3f**)	78	96–97 (0.30), [lit.[30] 93–94 (0.02)]	1.4525
1-bromo-3-methyl-1-butyne	8-methyl-(*E*)-6-nonen-1-ol (**3g**)	68	75–77 (0.25)	1.4484
1-bromo-2-cyclohexylethyne	7-cyclohexyl-(*E*)-6-hepten-1-ol (**3h**)	74	108–110 (0.25)	1.4807

[a] All reactions were carried out on a 30-mmol scale. [b] Isomeric purities of all products are ≥99% by capillary GC analysis. [c] Yields of pure distilled products. [d] Isolated yield from the corresponding alcohol.

Table IV. Stereospecific Synthesis of (*E*)-7-Alken-1-ols and Their Acetates from 1-Halo-1-alkyne and Borepane[a]

1-halo-1-alkyne	product[b]	yield, %	bp, °C (mm)	n^{20}_D
1-bromo-1-hexyne	(*E*)-7-dodecen-1-ol (**4a**)	80[c]	100–103 (0.8), [lit.[7a] 78–81 (0.06)]	1.4540 [lit.[7a] n^{25}_D 1.4521]
	1-acetoxy-(*E*)-7-dodecene (**4b**)	94[d]	93–95 (0.15), [lit.[7a] 78–82 (0.05)]	1.4420 [lit.[7a] n^{25}_D 1.4410]
1-bromo-1-octyne	(*E*)-7-tetradecen-1-ol (**4c**)	78[c]	107–109 (0.05), [lit.[7c] 110–115 (0.05)]	1.4555
	1-acetoxy-(*E*)-7-tetradecene (**4d**)	93[d]	115–117 (0.10), [lit.[7c] 90–95 (0.01)]	1.4460

[a] All reactions were carried out on a 30-mmol scale. [b] Isomeric purities were ≃99% by ^{13}C NMR analysis. [c] Yields of pure products isolated by distillation, based on borepane. [d] Isolated yields from the corresponding alcohols.

M solution), followed by the addition of iodine (30 mmol, 7.62 g) in tetrahydrofuran (30 mL). After 3 h, any excess iodine was decolorized by adding an aqueous solution of sodium thiosulfate, and the reaction mixture was allowed to warm to room temperature. The reaction mixture was oxidized in the usual way to provide, after distillation, (*Z*)-7-dodecen-1-ol (**2a**; 4.3 g, 78%), bp 115–117 °C (0.90 mm), n^{20}_D 1.4549 [lit.[29] bp 74–76 °C (0.01 mm)]. GC analysis showed >97% chemical purity. IR (neat): ν 3200 (—OH) and 1650 cm^{-1} (C=C). ^1H NMR ($CDCl_3$/TMS): δ 0.73–1.76 (m, 15 H), 1.78–2.43 (m, 4 H), 2.46 (s, 1 H, exchangeable with D_2O), 3.63 (t, J = 7 Hz, 2 H), and 5.23–5.59 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS): δ 129.87, 129.70 (C=C), 62.44, 32.65, 31.97, 29.76, 29.14, 27.15, 26.91, 25.72, 22.30, and 13.88.

1-Acetoxy-(*Z*)-7-dodecene (2b). Compound **2a** as obtained above was subjected to acetylation with acetyl chloride and pyridine in anhydrous benzene. Compound **2b** was obtained in 92% yield. IR (neat): ν 1651 (C=C) and 1745 cm^{-1} (—OAc). ^1H NMR ($CDCl_3$/TMS): δ 0.77–1.74 (m, 15 H), 1.78–2.22 (m, 7 H), 4.06 (t, J = 7 Hz, 2 H), and 5.19–5.50 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS): δ 170.62 (OC=O), 129.87, 129.44 (C=C), 64.33, 31.86, 29.49, 28.76, 28.56, 26.94, 26.81, 25.75, 22.21, 20.64, and 13.77.

(*Z*)-7-Tetradecen-1-ol (2c). IR (neat): ν 3320 (—OH) and 1650 cm^{-1} (C=C). ^1H NMR ($CDCl_3$/TMS): δ 0.69–1.75 (m, 19 H), 1.76–2.27 (m, 4 H), 2.36 (br s, 1 H, exchangeable with D_2O), 3.63 (distorted t, 2 H), and 5.21–5.51 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS): δ 129.87, 129.60 (C=C), 62.44, 32.64, 31.74, 29.70, 29.09, 28.93, 27.12, 25.69, 22.57, and 13.92.

1-Acetoxy-(*Z*)-7-tetradecene (2d). IR (neat): ν 1740 (—OAc) and 1651 cm^{-1} (C=C). ^1H NMR ($CDCl_3$/TMS): δ 0.70–1.81 (m, 19 H), 1.83–2.33 (m + s, 7 H), 4.08 (t, J = 7 Hz, 2 H), and 5.26–5.58 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS): δ 170.46 (*O*C=O), 129.91, 129.39 (C=C), 64.27, 31.73, 29.65, 29.54, 28.82, 28.56, 27.11, 26.91, 25.75, 22.52, 20.57, and 13.85.

Preparation of (*E*)-6-Nonen-1-ol (3a) is representative. In a dry, 250-mL flask were placed 1-iodo-1-butyne (6.62 g, 37 mmol) and tetrahydrofuran (15 mL). The solution was cooled to −78 °C, and borinane (30 mmol, 18 mL of a 1.66 M solution in tetrahydrofuran) was added slowly with stirring. After the addition, the mixture was stirred at −78 °C, followed by 2.5 h at 0 °C. Then sodium methoxide in methanol (60 mmol, 12.40 mL) was added dropwise at 0 °C, and the resulting mixture was stirred for 1 h at room temperature. The solvents were removed under reduced pressure. Tetrahydrofuran, methanol, and acetic acid (21 mL each) were introduced into the flask, and the contents were heated at 80–85 °C for 16 h. The reaction mixture was oxidized in the usual way to give (*E*)-nonen-1-ol (**3a**; 3.4 g, 80%), bp 84–85 °C (3 mm), n^{20}_D 1.4485 [lit.[30] bp 70–71 °C (0.05 mm), n^{23}_D 1.4493]. Capillary GC analysis showed >99% isomeric purity. IR (neat): ν 3339 (—OH) and 967 cm^{-1} (C=C). ^1H NMR ($CDCl_3$/TMS):

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δ 0.95 (t, J = 7 Hz, 3 H), 1.10–1.75 (m, 6 H), 1.80–2.22 (m, 5 H), 3.61 (q, J = 5 Hz, 2 H), and 5.29–5.50 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS): δ 131.97, 128.98 (C=C), 62.43, 32.43, 29.37, 25.46, 25.27, and 13.80. Mass spectrum: m/e (M^+) 142.

1-Acetoxy-(*E*)-6-nonene (3b). This compound was prepared by the reaction of acetic anhydride with **3a** in pyridine. Yield: 90%. Bp: 89–90 °C (3 mm), n^{20}_D 1.4352 [lit.[16] bp 65–70 °C (0.3 mm), n^{20}_D 1.4343]. Isomeric purity is >99% based on capillary GC. IR (neat): ν 1740 (C=O) and 967 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 0.95 (t, J = 7 Hz, 3 H), 1.20–1.79 (m, 6 H), 1.81–2.19 (m, 7 H), 4.05 (t, J = 7 Hz, 2 H), and 5.37–5.50 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS): δ 171.00 (C=O), 132.31, 128.94 (C=C), 64.57, 32.41, 29.29, 28.62, 25.63, 25.50, 20.92, and 13.98. Mass spectrum: m/e (M^+) 184.

(*E*)-6-Decen-1-ol (3c). IR (neat): ν 3390 (—OH), 1667, 979 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 0.86 (t, J = 7 Hz, 3 H), 1.20–1.70 (m, 8 H), 1.80–2.10 (m, 5 H), 3.60 (t, J = 5 Hz, 2 H), and 5.30–5.50 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS): δ 130.26, 130.13 (C=C), 62.69, 34.69, 32.54, 32.48, 29.42, 25.27, 22.70, and 13.55. Mass spectrum: m/e (M^+) 156.

(*E*)-6-Undecen-1-ol (3d). IR (neat): ν 3333 (—OH), 1654, 967 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 0.90 (t, J = 7 Hz, 3 H), 1.20–1.70 (m, 10 H), 2.0–2.2 (m, 5 H), 3.60 (t, J = 5 Hz, 2 H), and 5.25–5.40 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS): δ 130.07, 129.52 (C=C), 62.77, 32.66, 31.93, 29.54, 27.12, 26.91, 25.40, 22.28, and 13.91. Mass spectrum: m/e (M^+) 170.

(*E*)-6-Dodecen-1-ol (3e). IR (neat): ν 3332 (—OH), 1667, 967 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 0.88 (t, J = 7 Hz, 3 H), 1.13–1.75 (m, 12 H), 1.84–2.26 (m, 5 H), 3.60 (t, J = 5 Hz, 2 H), and 5.30–5.51 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS): δ 130.68, 130.01 (C=C), 62.87, 32.64, 32.54, 31.44, 30.89, 29.41, 25.27, 22.52, and 14.02. Mass spectrum: m/e (M^+) 184.

(*E*)-6-Tridecen-1-ol (3f). IR (neat): ν 3332 (—OH), 1650, 967 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 0.88 (t, J = 7 Hz, 3 H), 1.15–1.70 (m, 14 H), 1.80–2.20 (m, 5 H), 3.60 (t, J = 5 Hz, 2 H), and 5.30–5.45 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS): δ 130.75, 130.07 (C=C), 63.00, 32.63, 31.80, 29.66, 29.48, 28.89, 25.33, 22.70, and 14.09. Mass spectrum: m/e (M^+) 198.

8-Methyl-(*E*)-6-nonen-1-ol (3g). IR (neat): ν 3339 (—OH), 1668, 967 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 0.96 (d, J = 7 Hz, 6 H), 1.30–2.40 (m, 9 H), 2.70 (s, 1 H, exchangeable with D_2O), 3.56 (t, J = 5 Hz, 2 H), and centered at 5.33 (m, 2 H). Mass spectrum: m/e (M^+) 156.

7-Cyclohexyl-(*E*)-6-hepten-1-ol (3h). IR (neat): ν 3339 (—OH), 1668, 967 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 1.03–2.36 (m, 20 H), 3.60 (t, J = 5 Hz, 2 H), and centered at 5.30 (m, 2 H). Mass spectrum: m/e (M^+) 196.

The following procedure for the synthesis of (*E*)-7-dodecen-1-ol (**4a**) is representative. In a dry, 250-mL flask were placed *B*-chloroborepane[25] (30 mmol) and tetrahydrofuran (30 mL). The reaction flask was cooled to 0 °C, and lithium aluminum hydride (7.50 mmol, 7.50 mL of a 1 M solution in tetrahydrofuran) was added slowly with vigorous stirring. After 1 h, the resulting borepane solution was transferred into the solution of 1-bromo-1-hexyne (4.83 g, 30 mmol) in tetrahydrofuran (15 mL) at −78 °C. The reaction mixture was allowed to warm to 0 °C and then stirred for additional 3 h at 0 °C. Sodium methoxide in methanol (75 mmol, 16.60 mL) was added slowly at 0 °C, and the contents were stirred at room temperature for 1 h. Then, 3 mL of acetic acid was added to neutralize any excess of sodium methoxide, and the solvents were removed under reduced pressure. Acetic acid (40 mL) was added, and the reaction mixture was refluxed for 2 h. The reaction flask was brought to room temperature, and acetic acid was distilled off under vacuum. The reaction mixture was oxidized in the usual way to provide (*E*)-7-dodecen-1-ol (**4a**; 4.41 g, 80%), bp 100–103 °C (0.8 mm), n^{20}_D 1.4540 [lit.[7a] bp 78–81 °C (0.06 mm), n^{25}_D 1.4521]. GC analysis indicated >97% chemical purity. IR (neat): ν 3350 (—OH), 1650, 965 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 0.91 (distorted t, 3 H), 1.15–1.80 (m, 12 H), 1.81–2.30 (m + br s, 5 H), 3.61 (t, J = 6 Hz, 2 H), and 5.43 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS): δ 130.37, 130.12 (C=C), 62.88, 32.65, 32.47, 32.18, 31.80, 29.54, 28.91, 25.63, 22.10, and 13.79.

1-Acetoxy-(*E*)-7-dodecene (4b). Compound **4a** was treated with acetyl chloride and pyridine in anhydrous benzene to afford **4b** in 94% yield. IR (neat): ν 1740 (C=O), 1651, 967 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 0.90 (distorted t, 3 H), 1.10–1.81 (m, 12 H), 1.89–2.25 (m + s, 7 H), 4.08 (t, J = 7 Hz, 2 H), and 5.40 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS): δ 170.32 (*O*C=O), 130.29, 129.86 (C=C), 64.16, 32.28, 32.10, 31.67, 29.32, 28.52, 25.64, 21.98, 20.45, and 13.65.

(*E*)-7-Tetradecen-1-ol (4c). IR (neat): ν 3310 (—OH), 1650, 967 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 0.88 (distorted t, 3 H), 1.09–1.78 (m, 16 H), 1.83–2.29 (m, 5 H), 3.61 (t, J = 7 Hz, 2 H), and 5.39 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS): δ 130.49, 130.12 (C=C), 62.87, 32.73, 32.48, 31.74, 29.60, 28.82, 25.63, 22.59, and 14.00.

1-Acetoxy-(*E*)-7-tetradecene (4d). IR (neat): ν 1740 (C=O), 1650, 967 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 0.88 (distorted t, 3 H), 1.12–1.85 (m, 16 H), 1.9–2.28 (m + s, 7 H), 4.06 (t, J = 7 Hz, 2 H), and centered at 5.42 (m, 2 H).

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Registry No. **1a**, 68760-60-1; **1b**, 68760-59-8; **1c**, 90369-18-9; **1d**, 112043-59-1; **1e**, 112043-60-4; **2a**, 20056-92-2; **2b**, 14959-86-5; **2c**, 40642-43-1; **2d**, 16974-10-0; **3a**, 31502-19-9; **3b**, 30412-53-4; **3c**, 38421-92-0; **3d**, 16695-37-7; **3e**, 52957-14-9; **3f**, 37011-92-0; **3g**, 90369-20-3; **3h**, 112043-61-5; **4a**, 16695-40-2; **4b**, 16695-41-3; **4c**, 37011-95-3; **4d**, 28540-79-6; $CH_3(CH_2)_3C{\equiv}CH$, 693-02-7; $CH_3(CH_2)_2C{\equiv}CH$, 627-19-0; $(CH_3)_2CHC{\equiv}CH$, 598-23-2; $(CH_3)_3CC{\equiv}CH$, 917-92-0; $CH_3CH_2C{\equiv}CI$, 66794-29-4; $CH_3(CH_2)_2C{\equiv}CBr$, 14752-60-4; $CH_3(CH_2)_3C{\equiv}CBr$, 1119-64-8; $CH_3(CH_2)_4C{\equiv}CBr$, 19821-84-2; $CH_3(CH_2)_5C{\equiv}CBr$, 38761-67-0; $(CH_3)_2CHC{\equiv}CBr$, 54105-74-7; $CH_3(CH_2)_5C{\equiv}CH$, 629-05-0; cyclohexylethyne, 931-48-6; borinane, 289-53-2; *B*-chloroborepane, 60579-52-4; 1-bromo-2-cyclohexylethyne, 66684-39-7.