(m, 4 H, $CH_2C(O)CH_2$). ^{13}C NMR ($CDCl_3$): δ 210.57, 42.38, 35.79, 31.46, 23.64, 22.42, 13.81, and 7.80. Mass spectrum: *m/e* M^+ 128.

2,2-Dimethyl-3-octanone (5f). IR (neat): δ 1705 cm^{-1} (–C(O)–). ^1H NMR ($CDCl_3$): δ 0.90 (distorted t, 3 H, 1 × CH), 1.16 (s, 9 H, 1 × $C(CH_3)_3$, 1.23–2.00 (m, 6 H, 3 × CH_2), and 2.46 (t, J = 7 Hz, 2 H, $CH_2C(O)$–). ^{13}C NMR ($CDCl_3$): δ 196.57, 44.01, 36.36, 31.54, 26.37, 23.61, 22.51, and 13.84. Mass spectrum: *m/e* M^+ 156.

Pheromones via Organoboranes. 2. Vinylic Organoboranes. 8. Applications of the General Stereoselective Synthesis of (*E*)-Disubstituted Alkenes via Thexylchloroborane–Dimethyl Sulfide to the Synthesis of Pheromones Containing an (*E*)-Alkene Moiety

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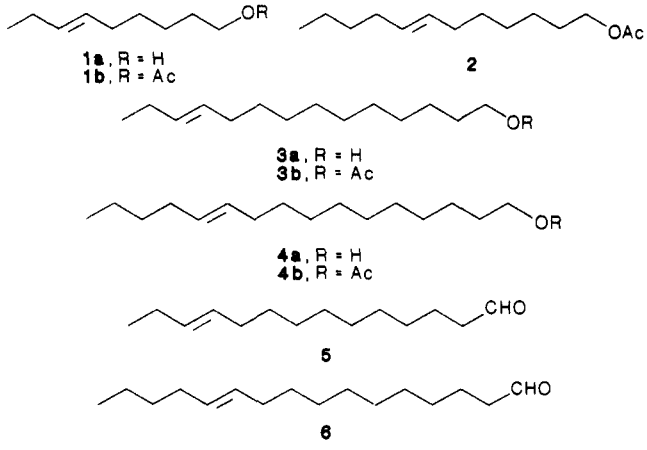
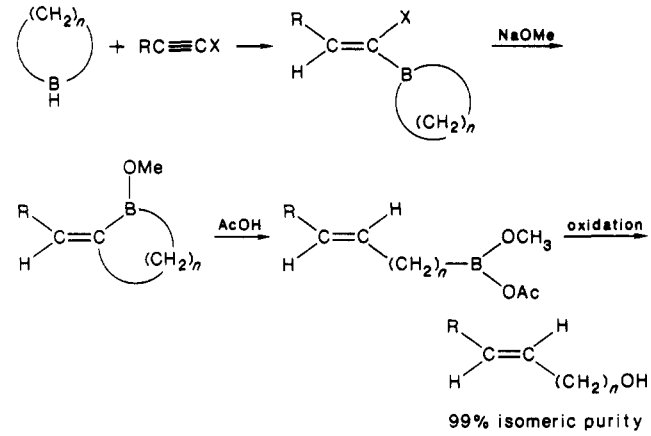
Various (*E*)-pheromones of the general structures (*E*)-X-alken-1-yl acetates, (*E*)-X-alken-1-ols, and (*E*)-X-alken-1-als have been prepared via thexylchloroborane–dimethyl sulfide (ThxBHCl·SMe_2). Hydroboration of acetate-functionalized alkenes with ThxBHCl·SMe_2 gives cleanly the corresponding thexylalkylchloroboranes (ThxBRCl, B). Hydridation of B with potassium triisopropoxyborohydride (KIPBH) at –78 °C gives cleanly the corresponding thexylalkylboranes (ThxBRH, C). These are quenched immediately with 1-halo-1-alkynes to give *B*-(*cis*-1-halo-1-alkenyl)thexylalkylboranes (D). Treatment of D with sodium methoxide results in the displacement of bromine by the alkyl group on boron to produce *B*-(*trans*-1-alkyl-1-alkenyl)thexylborinates (E). Protonolysis of E with acetic acid provides (*E*)-X-alken-1-yl acetates in high yields and in >99% isomeric purities. Treatment of (*E*)-X-alken-1-yl acetates with base affords the corresponding (*E*)-X-alken-1-ols. Oxidation of (*E*)-X-alken-1-ols with dimethyl sulfoxide activated by oxalyl chloride or the complex of dimethyl sulfide and chlorine produces (*E*)-X-alken-1-als quantitatively. By properly choosing the starting functionalized alkenes and 1-halo-1-alkynes, various (*E*)-pheromones can be prepared easily. The present procedure appears to be general. There does not appear to be any limitation on the length of the carbon chain or the position of the double bond in the target molecules.

Many sex pheromones produced by moth and butterfly species (Lepidoptera) are straight-chain functionalized (*E*)-alkenes[2] of the general structures (*E*)-X-alken-1-ols, (*E*)-X-alken-1-yl acetates, or (*E*)-X-alken-1-als. Examples are (*E*)-6-nonen-1-ol (**1a**) from the male Mediterranean fruitfly (*Ceratitis capitata*),[3a] (*E*)-6-nonen-1-yl acetate (**1b**),



Scheme I



the attractant for the female melonfly (*Daucus cucurbitae*),[3b] (*E*)-7-dodecen-1-yl acetate (**2**) from the female false coddling moth (*Cryptophlebia leucotreta*),[3c] (*E*)-11-tetradecen-1-ol (**3a**) and its corresponding acetate (**3b**) from

(1) (a) Postdoctoral research associate on a grant from Albany International Chemical Division. (b) Postdoctoral research associate, Purdue University.

(2) (a) Brand, J. M.; Young, J. C.; Silverstein, R. M. *Fortschr. Chem. Org. Natur.* **1980**, *37*, 1–190. (b) Henrich, C. A. *Tetrahedron* **1977**, *33*, 1845. (c) Rossi, R. *Synthesis* **1977**, 817; (d) **1978**, 413. (e) Shorey, H. H.; McKelvey, J. J. *Chemical Control of Insect Behavior. Theory and Application*; John Wiley & Sons: New York, 1977. (f) Mori, K. "The Synthesis of Insect Pheromones" in *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; John Wiley & Sons: New York, 1981; Vol. 4, pp 1–183.

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the female fruittree leafroller (*Archips argyrospilus*),[3e] tufted apple budmoth (*Platynota idaensalus*),[3e] and omnivorous leafroller (*Plalynota slultana*).[3f] In addition, (*E*)-11-hexadecen-1-ol (**4a**) and its corresponding acetate (**4b**) are pheromones of *Brachmia macroscopa*.[3g] Two examples containing the aldehyde functionality are (*E*)-11-tetradecen-1-al (**5**) from the female western spruce budworm (*Choristoneura occidentalis*)[3h] and (*E*)-11-hexadecen-1-al (**6**) from the corn earworm (*Heliothis zea*).[3i]

The characteristic structure variation of these pheromones is displayed through differences in the carbon chain length, double bond position, or the functional moieties. It is now known that the purity or the ratio of isomers (*E*:*Z*) has marked effect on the attraction of insects.[2e] Therefore, synthetic procedures that achieve stereospecific synthesis of such compounds are desirable.

Many reactions of organoboranes are highly stereospecific.[4] Therefore, it appeared that procedures based on organoborane chemistry should be especially favorable for such syntheses. In fact, we have previously demonstrated that by applying boracyclanes, some (*E*)-alken-1-ols can be obtained easily in high stereochemical purities[5] (Scheme I).

Unfortunately, this procedure is limited by the availability of the boracyclanes; only borinane and borepane are readily available and have been used to prepare (*E*)-6-alken-1-ols[5b] and (*E*)-7-alken-1-ols,[5a] respectively.

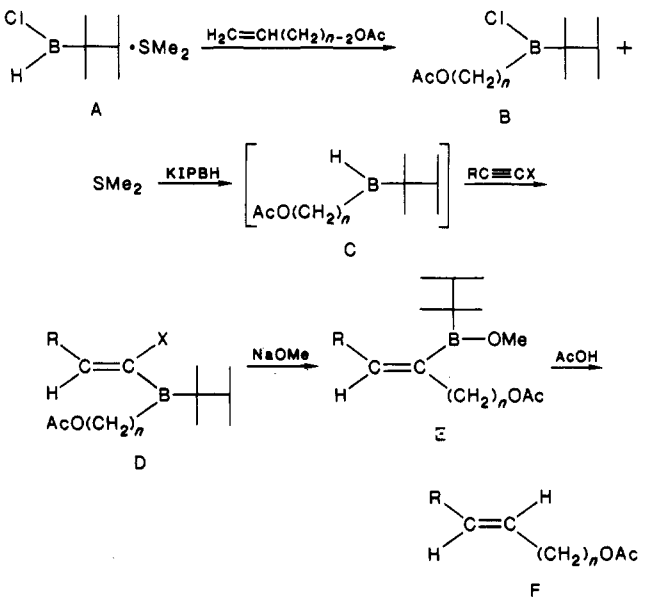
Recently, the monohydroboration of terminal reactive alkenes[6] and the preparation of unbranched disubstituted (*E*)-alkenes have become possible by the use of thexylchloroborane–dimethyl sulfide (ThxBHCl·SMe_2).[7] It appeared that this newly developed reagent should be ideal for providing a general synthesis of (*E*)-pheromones. This paper reports the successful general synthesis of such compounds via ThxBHCl·SMe_2 (Scheme II).

^{11}B NMR was first used to follow the hydroboration of the model compound, 5-hexen-1-yl acetate, by ThxBHCl·SMe_2. When 1 equiv of ThxBHCl·SMe_2 was added to 10 mmol of 5-hexen-1-yl acetate in methylene chloride at 0 °C, followed by stirring of the resulting solution at room temperature for 1 h, the ^{11}B NMR of the product solution indicated the complete disappearance of the starting ThxBHCl·SMe_2 (δ 7.4) with the formation of a pure (>97%) dialkylchloroborane species (δ 79.1). After methanolysis, ^{11}B NMR spectra showed a very clean (>95%) conversion of this product to a dialkylborinate species (δ 54.5). These results clearly indicate that ThxBHCl·SMe_2 hydroborates alkenyl acetates cleanly to give a thexylalkylchloroborane intermediate (B) and the acetate functionality in the starting alkenes does not interfere with the hydroboration.

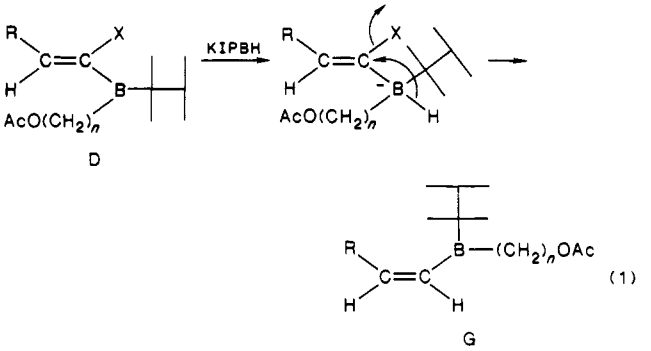
Further evidence for the clean formation of pure B was provided by the high yield isolation (90%) of pure 1,6-hexanediol (mp 43–45 °C, >99% pure) after oxidation with alkaline hydrogen peroxide. The absence of 1,5-hexanediol reconfirmed that ThxBHCl·SMe_2 is a highly regioselective hydroborating agent.[6]

Clean hydridation of B with potassium triisopropoxyborohydride (KIPBH)[8-10] free from disproportionation of the resulting thexylalkylborane (C) and its subsequent clean hydroboration of the haloalkyne to give *B*-(*cis*-1-halo-1-alkenyl)thexylalkylborane (D) were achieved by performing the hydridation at −78 °C (instantaneously), followed by quenching the resulting thexylalkylborane immediately with the haloalkyne.

Scheme II



It should be noted that an attempt to avoid disproportionation by conducting the hydridation in the presence of haloalkyne was not successful. Intermediate D thus formed competes strongly with thexylalkylchloroborane for the hydride to form a stable *cis*-vinylborane side product (G)[11] (eq 1).



Intermediate D, prepared according to Scheme II, was then treated with sodium methoxide in methanol to obtain the *B*-(*trans*-1-alkyl-1-alkenyl)thexylborinate (E).[12] Evidence for the fairly clean formation of E was provided by

(4) (a) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975. (b) Brown, H. C. *Pure Appl. Chem.* **1976**, *47*, 49. (c) Mikhailov, B. M.; Bubnov, Y. N. *Organoboron Compounds in Organic Synthesis*; Revised Engl. Ed., Bell and Bain Ltd., Glasgow, 1984.

(5) (a) Basavaiah, D. *Heterocycles* **1982**, *18*, 153. (b) Brown, H. C.; Basavaiah, D.; Singh, S. M. *Synthesis* **1984**, 920.

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(7) Brown, H. C.; Lee, H. D.; Kulkarni, S. U. *Synthesis* **1982**, 195.

(8) KIPBH in THF was prepared from potassium hydride and triisopropoxylborane, following the literature procedure (ref 9), except the reaction was done at 0 °C and the prepared reagent was kept at that temperature for use. Potassium tetraisopropoxyborate (4–6%) was found as an impurity by this preparation. Preparation of pure KIPBH (≥99%) has recently been developed (ref 10).

(9) Brown, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 4100.

(10) Brown, H. C.; Nazer, B.; Sikorski, J. A. *Organometallics* **1983**, *2*, 634.

(11) Actually, in one case we have isolated ~40% of an aldehyde, RCH_2CHO, from the corresponding *cis*-vinylborane intermediate (G) after oxidation with phosphate-buffered hydrogen peroxide.

(12) It was previously established that in base-induced migration of the alkyl group from boron to the bromine-bearing carbon, the migrating group and the alkyl group of the original alkyne are trans to each other (Scheme II): see ref 7 and the references cited therein.

Table I. Preparation of (*E*)-Pheromones with Acetate Functionality from Alkenyl Acetates and Haloalkynes

alkenyl acetate	haloalkyne	pheromone[a]	yield,[b] %	bp °C/mm	n^{20}_D
4-penten-1-yl acetate	1-iodo-1-butyne	**1b**	74	79–82/0.15	1.4410
5-hexen-1-yl acetate	1-bromo-1-hexyne	**2**	84	86–88/0.005	1.4426
9-decen-1-yl acetate	1-bromo-1-butyne	**3b**	79	124–128/0.01	1.4475
9-decen-1-yl acetate	1-bromo-1-hexyne	**4b**	83	123–127/0.005	1.4494

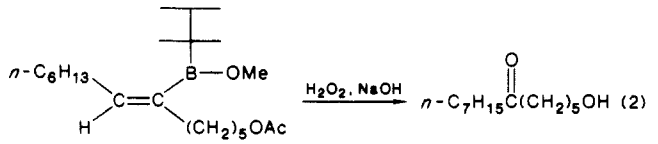
[a] Chemical purities by GC are >97%. All products showed the characteristic infrared absorption at ~970 cm^{-1}. ^{13}C NMR detected no signals derived from the corresponding *Z* isomers. Other spectral data are all consistent with the structures expected. [b] Yield of isolated products based on 1-halo-1-alkyne.

Table II. Preparation of (*E*)-Pheromones with Alcohol Functionality from the Corresponding Acetates

pheromone[a]	bp °C/mm	yield,[b] %	n^{20}_D
1a	80–84/0.2	96	1.4478
3a	98–101/0.02	98	1.4458
4a		97	1.4563

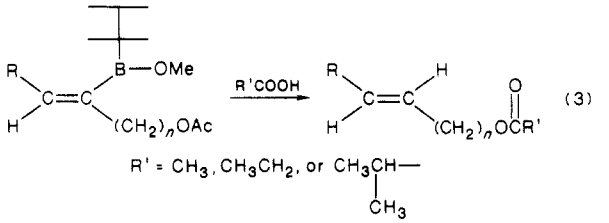
[a] All products gave satisfactory spectral data. [b] Based on the corresponding acetates. Products were isolated by evaporating solvents under high vacuum and were >98% pure by GC analysis. Due to physical loss, yields are lower after distillation.

the isolation of a keto alcohol in good yield (81%) following oxidation with alkaline hydrogen peroxide (eq 2).



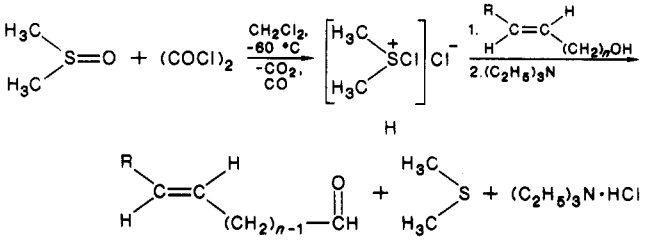
E

Thexylalkenylborinates were known to undergo protonolysis with considerable difficulty.[4a,13] It was previously suggested that isobutyric acid or propionic acid other than acetic acid to be used so that protonolysis could be conducted at higher reflux temperatures for a shorter reaction time.[13] However, attempts to react E with these acids afforded only the corresponding isobutyrate or propionate. Apparently protonolysis was accompanied by an undesired transesterification (eq 3).



Fortunately, we found that protonolysis with acetic acid presents no difficulty. Even though a longer time (up to 20 h) was needed to complete the reaction, no isomerization of the double bond was detected by examining the spectroscopic data of all the products. Consequently, (*E*)-7-dodecen-1-yl acetate (**2**), the pheromone from the female false coddling moth, was prepared from 5-hexen-1-yl acetate and 1-bromo-1-hexyne in 84% yield. The trans geometry of the double bond was confirmed by the appearance of the characteristic infrared absorption at 970 cm^{-1}. Further evidence for this trans stereochemistry was provided by the only two signals (δ 130.0 and 130.5) for two vinylic carbons (nonequivalent) found in the ^{13}C NMR spectrum of this product.[14] Our results for the synthesis of these (*E*)-pheromones containing an acetate group are summarized in Table I.

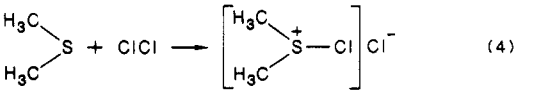
Scheme III



Alcoholic pheromones were obtained quantitatively by hydrolysis of the corresponding acetates with base. These pheromones are summarized in Table II.

One way to prepare pheromones with aldehyde functionality would be to construct the corresponding alcohols of the needed carbon skeletons, followed by oxidation of these alcohols to the aldehydes. The most general procedure for this purpose found in the literature is the oxidation with chromium trioxide and pyridinium chloride.[15] Low to moderate yields are generally observed with this oxidation. The clean oxidation with dimethyl sulfoxide, activated by oxalyl chloride,[16] does not appear to have been applied to the synthesis of pheromones (Scheme III). Accordingly, we carried out this reaction to see if this reaction could be used to prepare these pheromones with aldehyde functionality. Indeed, by following the literature procedure, essentially quantitative yields of the aldehydes were obtained. For example, (*E*)-11-hexadecen-1-al (**6**), the pheromone from the corn earworm, was prepared in 98% yield from the corresponding alcohol. The trans stereochemistry of this product was again detected by the presence of the typical infrared absorption at 980 cm^{-1} and by the single signal (δ 130.3) of the two vinylic carbons (equivalent) found in the ^{13}C NMR of this product.[14] However, there is one possible difficulty with this procedure. Oxalyl chloride reacts vigorously and exothermically with dimethyl sulfoxide, even at −60 °C.[16] Therefore, this procedure might not be suitable for large-scale preparations.

The same oxidation was also carried out by using the same chlorosulfonium intermediate (H), but prepared directly from dimethyl sulfide and chlorine[17] (eq 4).



Preparation of this intermediate at −78 °C (instantaneously), followed by reaction with the alcohol at −78 °C or −60 °C, provided essentially quantitative yields of al-

(13) Negishi, E.; Katz, J.-J.; Brown, H. C. *Synthesis* **1972**, 555.
(14) In a mixture of isomers, the vinylic carbons of trans configuration can be distinguished from the corresponding carbons of cis configuration: Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757.
(15) (a) Nesbitt, B. F.; Beevor, P. S.; Hall, D. R.; Lester, R.; Dyck, V. A. *J. Insect. Physiol.* **1975**, *21*, 1883. (b) Kondo, K.; Negishi, A.; Tunemoto, D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 407. (c) Fyles, T. M.; Leznoff, C. C.; Weatherston, J. *Can. J. Chem.* **1978**, *56*, 1031.
(16) (a) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651. (b) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480. (c) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.
(17) Corey, E. J.; Kim, C. U. *J. Am. Chem. Soc.* **1972**, *94*, 7586.

Table III. Preparation of (*E*)-Pheromones with Aldehyde Functionality from the Corresponding Alcohols

alcohol,[a] mmol	reagent, mmol	pheromone[b]	yield,[c] %	n^{20}_D
(*E*)-11-tetradecen-1-ol (3.4)	Me_2SO/oxalyl chloride (5.0)	**5**	97	1.4483
(*E*)-11-tetradecen-1-ol (3.4)	DMS/Cl_2 (5.0)	**5**	97	1.4480
(*E*)-11-hexadecen-1-ol (3.2)	Me_2SO/oxalyl chloride (5.0)	**6**	98	1.4494
(*E*)-11-hexadecen-1-ol (3.2)	DMS/Cl_2 (5.0)	**6**	98	1.4501

[a] Alcohols were added as a solution in CH_2Cl_2 (10 mL). [b] Products isolated by extraction with pentane. Pentane extracts were combined, dried, and evaporated under high vacuum. Chemical purity of the products are >98%. All products gave satisfactory spectral data. The characteristic infrared absorption at ~970 cm^{-1} was detected in all products. ^{13}C NMR spectra detected no signals from the corresponding *Z* isomers. [c] Based on the corresponding alcohols.

dehydes.[18] Since preparation of the sulfonium intermediate from dimethyl sulfide and chlorine is instantaneous and quantitative, but not especially vigorous at −78 °C, this procedure appears to be the procedure of choice for large-scale preparation. Results on the synthesis of pheromones containing an aldehyde group are summarized in Table III.

Conclusion

Organoborane chemistry provides a versatile approach to organic synthesis. However, only relatively few of these reactions have been applied in the recent past to the synthesis of natural products. We have undertaken the present program to provide a general synthesis of pheromones to demonstrate the efficiency of the procedure. Essentially, the one-pot synthesis, which affords the desired (*E*)-pheromones containing an acetate group in high yield, with a defined configuration, promises to make this a very useful procedure for the synthesis of this type of compound. Pheromones containing alcohol groups can easily be obtained from the corresponding acetates by simple hydrolysis with base. Hydroboration to assemble the carbon skeletons of the target molecules, followed by oxidation of the functional group, provides an easy route for the synthesis of pheromones containing the aldehyde group. The present procedure appears to be general, more general than synthesis with the boracyclanes.[5] There appears to be no limitation with regard to the carbon-chain length, nor the position of the double bond in the products. It should also be mentioned that our procedure, which achieves the monohydroboration of terminal alkenes with ThxBHCl·SMe_2[6] and the subsequent conversion to unbranched (*E*)-pheromones, has not been available previously. We are now exploring the synthetic application of this reagent for other synthesis.

Experimental Section

General. The reaction glassware required for the experiments were predried at 140 °C for several hours, assembled hot, and cooled under a stream of prepurified nitrogen. Syringes were assembled and fitted with needles while hot and then cooled. All reactions were carried out under a static pressure of nitrogen in flasks fitted with septum-covered side arms using standard techniques for handling air-sensitive materials.[1a] GC analysis was performed on a Varian 1200 gas chromatograph on a 6 ft × $^1/_8$ in. column in 5% or 10% SE-30. ^1H NMR spectra were recorded on a Varian T-60 spectrometer. ^{13}C and ^{11}B NMR spectra were recorded on a Varian FT-80 spectrometer. All ^1H and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane (δ 0). All ^{11}B NMR chemical shifts are reported relative to BF_3·OEt_2 (δ 0) with the chemical shifts downfield from BF_3·OEt_2 assigned as positive. Infrared spectra were recorded on a Perkin-Elmer 137 sodium chloride spectrophotometer. Elemental analysis data and mass spectra were obtained from Microanalysis Laboratory and Mass Spectrometry Center of Purdue University respectively.

Materials. The starting materials of alkenes and alkynes were purchased from Chemical Samples Company. THF was distilled from lithium aluminum hydride and stored under nitrogen prior to use. Methylene chloride was degassed and stored over 3-Å molecular sieves. Methyl sulfide was distilled from a small amount of 9-BBN and stored under nitrogen. Dimethyl sulfoxide was distilled from calcium hydride under reduced pressure and stored over 3-Å molecular sieves. Starting alkenyl acetates were prepared from the corresponding alcohols by reacting with acetic anhydride catalyzed by pyridine. 1-Halo-1-alkynes were prepared according to the literature procedure.[19] Solutions of ThxBHCl·SMe_2 in CH_2Cl_2 were prepared and standardized as described elsewhere.[6] Potassium triisopropoxyborohydride (KIPBH) was prepared according to the literature procedure,[9] except that the addition of potassium hydride to triisopropoxyborane in THF was done at 0 °C. A solution of chlorine in CH_2Cl_2 was prepared by first condensing Cl_2 at −78 °C in a measuring vessel, followed by evaporating it into a flask containing a known amount of CH_2Cl_2. The solution was standardized[20] and used immediately after its preparation.

(*E*)-6-Nonen-1-yl Acetate (1b). To a solution of 4-penten-1-yl acetate (3.85 g, 30 mmol) in CH_2Cl_2 (20 mL) in a 250-mL flask was added at 0 °C under nitrogen a solution of ThxBHCl·SMe_2 in CH_2Cl_2 (13.7 mL, 2.2 M). The mixture was stirred for 90 min at room temperature, cooled to −78 °C, and diluted with THF (50 mL). To the well-stirred solution was added a 0.77 M solution of freshly prepared KIPBH (39.0 mL, 30 mmol; also cooled to −78 °C). The mixture was thoroughly stirred for 10 min, 1-iodo-1-butyne (4.50 g, 30 mmol) was added, and again the mixture was mixed well. After 10 min, the flask was brought up to −25 °C and maintained at this temperature for 2 h with vigorous stirring. To the reaction mixture was added dropwise a 4.4 M solution of sodium methoxide in methanol (10.2 mL, 45 mmol) and the mixture was allowed to warm up to room temperature while stirring. After 1 h, the flask was cooled with an ice bath, with the addition of a 1.1 M solution of hydrochloric acid in ethyl ether (13.6 mL, 15 mmol). The solvents and low boiling materials were removed under aspirator vacuum, acetic acid (60 mL) was added, and the mixture was heated under reflux temperature for 20 h. The cooled mixture was poured into water (200 mL) and extracted with pentane. The combined pentane extracted was washed with saturated K_2CO_3 solution and dried (K_2CO_3). Distillation provided (*E*)-6-nonen-1-yl acetate (**1b**), 4.08 g (74%), bp 79–82 °C (0.15 mm), n^{20}_D 1.4410. GC analysis indicated >97% chemical purity. IR (neat): 1739 (C=O), 1239 (CO), 967 cm^{-1} (*trans*-CH=CH—). ^1H NMR: δ 0.95 (t, 3 H, *J* = 7.0 Hz), 1.12–1.76 (m, 6 H), 1.76–2.28 (m + s, 7 H), 4.02 (t, 2 H, *J* = 6.0 Hz), 5.42 (m, 2 H). ^{13}C NMR: δ 14.0, 20.9, 25.5, 25.6, 28.6, 29.3, 32.4, 64.6, 128.9, 132.3, 171.0. Mass spectrum (chemical ionization with isobutane): *m/e* 185 (m + H), 125 (m + H − AcOH). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.58; H, 10.76.

(*E*)-7-Dodecen-1-yl Acetate (2). This was prepared according to the method described above. **2** (5.69 g, 84%) was obtained by distillation, bp 86–88 °C (0.005 mm), n^{20}_D 1.4426. GC analysis indicated >98% chemical purity. IR (neat): 1740 (C=O), 1240 (CO), 970 cm^{-1} (*trans*-CH=CH—). ^1H NMR: δ 0.66–1.68 (m,

(18) According to the original procedure, chlorine and dimethyl sulfide were mixed at 0 °C and oxidation of cyclohexanol was conducted at −25 °C; ~80% of cyclohexanone was obtained. The less than quantitative yield observed here might be due to the instabilities of the sulfonium intermediates at that reaction temperature.

(19) 1-Bromo-1-hexynes were prepared by the method of Schulte and Goes: Schulte, K. E.; Goes, M. *Arch. Pharm.* **1959**, *290*, 118. 1-Iodo-1-alkynes were prepared by the action of *n*-BuLi on the corresponding 1-alkynes followed by treatment with iodine.

(20) Furman, N. H. *Standard Methods of Chemical Analysis*, 6th ed.; D. Van Nostrand Company: Princeton, New Jersey, 1962; p 333.

15 H), 1.68–2.26 (m + s, 7 H), 4.00 (t, 2 H, J = 6.6 Hz), 5.40 (m, 2 H). ^{13}C NMR: δ 13.8, 20.9, 22.1, 25.7, 28.6, 29.4, 30.8, 31.8, 32.2, 32.4, 64.5, 130.0, 130.5, 170.7. Mass spectrum (chemical ionization): m/e 227 (m + H), 167 (m + H - AcOH).

(*E*)-11-Tetradecen-1-yl acetate (3b) was prepared according to the procedure described for **1b**. 6.03 g (79%) of **3b** (6.03 g, 79%) was obtained by distillation, bp 124–128 °C (0.01 mm), n^{20}_D 1.4475. GC analysis indicated >98% chemical purity. IR (neat): 1740 (C=O), 1240 (CO), 970 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.86 (t, 3 H, J = 7.8 Hz), 1.04–1.66 (m, 16 H), 1.66–2.14 (m + s, 7 H), 3.94 (t, 2 H, J = 7.2 Hz), 5.32 (m, 2 H). ^{13}C NMR: δ 13.9, 20.9, 25.6, 25.9, 28.7, 29.1, 29.2, 29.5, 29.7, 30.8, 32.5, 64.6, 129.3, 131.9, 170.5. Mass spectrum (chemical ionization): m/e 255 (m + H), 195 (m + H - AcOH).

(*E*)-11-Hexadecen-1-yl acetate (4b) was prepared according to the procedure described for **1b**. **4b** (7.05 g, 83%) was obtained by distillation, bp 123–127 °C (0.005 mm), n^{20}_D 1.4494. GC analysis indicated >97% chemical purity. IR (neat): 1741 (C=O), 1238 (CO), 970 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.64–1.72 (m, 23 H), 1.72–2.28 (m + s, 7 H), 3.96 (t, 2 H, J = 6.6 Hz), 5.38 (m, 2 H). ^{13}C NMR: δ 13.8, 20.6, 22.1, 25.9, 28.6, 29.1, 29.2, 29.4, 29.6, 31.8, 32.2, 32.5, 64.3, 130.2, 170.5. Mass spectrum (chemical ionization): m/e 283 (m + H), 223 (m + H - AcOH).

(*E*)-6-Nonen-1-ol (1a). To a mixture of aqueous NaOH (20% solution, 50 mL, 250 mmol) and 95% ethanol (50 mL) in a 250-mL beaker at room temperature was added (*E*)-6-nonen-1-yl acetate (2.7 g, 15 mmol). The mixture was further stirred for 30 min. The mixture was then extracted with pentane, washed with saturated NaCl solution, and dried (K_2CO_3). Removal of solvent under vacuum gave 2.04 g (97%) of **1a**. GC analysis indicated >98% chemical purity. Distillation provided 1.83 g (86%) of pure **1a**, bp 80–84 °C (0.2 mm), n^{20}_D 1.4478. IR (neat): 3300 (OH), 1126 (CO), 965 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.94 (t, 3 H, J = 6.8 Hz), 1.10–1.68 (m, 6 H), 1.68–2.20 (m, 4 H), 2.88 (br, 1 H, OH), 3.36 (t, 2 H, J = 6.6 Hz), 5.40 (m, 2 H). ^{13}C NMR: δ 13.8, 25.3, 25.5, 29.4, 32.4, 62.4, 129.0, 132.0. Mass spectrum (chemical ionization): m/e 143 (m + H), 125 (m + H - H_2O).

(*E*)-11-Tetradecen-1-ol (3a) was prepared according to the procedure described above. **3a** (3.12 g, 98%) was obtained from the extracts. GC analysis indicated >97% chemical purity. Distillation provided 2.70 (85%) of pure **3a**, bp 98–101 °C (0.02 mm), n^{20}_D 1.4558. IR (neat): 3220 (OH), 1070 (CO), 980 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.88 (t, 3 H, J = 7.6 Hz), 1.02–1.68 (m, 16 H), 1.68–2.20 (m, 4 H), 2.82 (br, 1 H, OH), 3.58 (t, 2 H, J = 6.4 Hz), 5.32 (m, 2 H). ^{13}C NMR: δ 13.7, 25.4, 25.9, 29.2, 29.3, 29.6, 32.5, 32.6, 61.7, 129.0, 131.5. Mass spectrum (chemical ionization): m/e 213 (m + H), 195 (m + H - H_2O). Anal. Calcd for C, 79.16; H, 13.28. Found: C, 79.00; H, 13.35.

(*E*)-11-Hexadecen-1-ol (4a) was prepared according to the procedure described for **1a**. **4a** (3.49 g, 97%) was obtained after removing the solvent under vacuum. This product was essentially chemically pure (>98% by GC analysis), n^{20}_D 1.4563. IR (neat): 3300 (OH), 1070 (CO), 980 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.64–1.68 (m, 23 H), 1.68–2.20 (m, 4 H), 2.74 (br, 1 H, OH), 3.60 (t, 2 H, J = 6.2 Hz), 5.38 (m, 2 H). ^{13}C NMR: δ 13.8, 22.1, 25.7, 29.1, 29.5, 30.8, 31.8, 32.2, 32.5, 32.7, 62.8, 131.3. Mass spectrum (chemical ionization): m/e 241 (m + H), 223 (m + H - H_2O).

(*E*)-11-Tetradecen-1-al (5). Method A. The literature procedure[16] was basically followed. A carefully dried 50-mL flask fitted with a septum inlet and a magnetic stirring bar was attached to a mercury bubbler. In the flask was placed oxalyl chloride (0.45 mL, 5 mmol) in CH_2Cl_2 (10 mL). The contents of the flask were cooled to −60 °C. Me_2SO in CH_2Cl_2 (4.5 mL, 1.1 M) was then added dropwise. Stirring was continued for 5 min, followed by the addition of (*E*)-11-tetradecen-1-ol (1 mL, 3.4 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 15 min, followed by the addition of triethylamine (1.4 mL, 10 mmol). After 5 min, the cooling bath was removed, and the mixture was further stirred while the temperature was allowed to warm to room temperature in 30 min. Vacuum was applied to remove the solvent and low boiling materials. The residue was again digested with pentane (total 30 mL). Ammonium salt remained undissolved and was filtered off. Pentane was removed by evaporation under vacuum. Oily (*E*)-11-tetradecen-1-al (**5**) (0.69 g, 97%) was collected without further purification. GC analysis indicated >98% chemical purity, n^{20}_D 1.4483. IR (neat): 2700 (C(O)H), 1720 (C=O), 977 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.95 (t, 3 H, J = 7.2 Hz), 1.12–1.68 (m, 14 H), 1.68–2.62 (m, 6 H), 5.40 (m, 2 H), 9.74 (m, 1 H). ^{13}C NMR: δ 14.0, 22.1, 25.6, 29.2, 29.4, 29.7, 30.9, 32.5, 43.9, 129.3, 131.9, 202.3. Mass spectrum (chemical ionization): m/e 211 (m + H), 209 (m - H), 193 (m + H - H_2O).

Method B.[17,18] Chlorine in CH_2Cl_2 (0.4 M, 12.5 mL) cooled to −78 °C in a flask was transferred with a double-ended needle to a solution of dimethyl sulfide in CH_2Cl_2 (0.5 M, 10 mL) also cooled to −78 °C. The mixture was stirred for 5 min followed by the addition of 3.4 mmol of (*E*)-11-tetradecen-1-ol. The mixture was stirred for 15 min, followed by the addition of triethylamine (1.4 mL, 10 mmol). After 5 min, the cooling bath was removed and the mixture was further stirred while the temperature was allowed to warm to room temperature in 30 min. The product was worked up as described above to give 0.69 g (97%) of **5**. GC analysis indicated >98% chemical purity, n^{20}_D 1.4480. Spectral data completely agreed with the above one.

(*E*)-11-Hexadecen-1-al (6) was prepared according to method A described for **5**; 0.75 g (98%) was obtained. GC analysis indicated >98% chemistry purity, n^{20}_D 1.4494. IR (neat): 2705 (C(O)H), 1730 (C=O), 980 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.66–1.70 (m, 21 H), 1.70–2.58 (m, 6 H), 5.38 (m, 2 H), 9.76 (m, 1 H). ^{13}C NMR: δ 13.9, 22.2, 29.1, 30.0, 30.8, 31.9, 32.3, 32.6, 43.9, 130.3, 202.6. Mass spectrum (chemical ionization): m/e 239 (m + H), 237 (m - H), 221 (m + H - H_2).

This compound was also prepared according to method B described for **5**. Similar results were obtained. Yield: 0.75 g (98%), n^{20}_D 1.4501. Other spectral data were completely consistent with those of **6** prepared above.

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Synthesis of (*E*)-(2-Arylethenyl)silanes by Palladium-Catalyzed Arylation of Vinylsilanes in the Presence of Silver Nitrate

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A series of (*E*)-trimethyl(2-arylethenyl)silanes **1–16** and (*E*)-triethoxy(2-arylethenyl)silanes **17** and **18** has been synthesized by palladium-catalyzed arylation of the corresponding vinylsilanes, in the presence of silver nitrate. Apart from enhancing the rate of the reaction, silver nitrate also completely suppresses the desilylation. In the absence of silver salt, under ordinary Heck arylation conditions, styrene derivatives are formed in good yields. A possible mechanistic rationale for the formation of styrenes is discussed.

Vinylsilanes have become increasingly important intermediates for synthesis.[1-3] We have utilized vinyltrimethylsilane as an ethylene equivalent for the preparation of styrene derivatives from aryl iodides (eq 1).[4] Silver salt

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