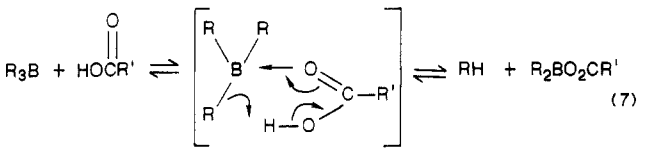
through a six-membered transition state where the nucleophilic and electrophilic sites are in proper geometric relationship to one another (eq 7).[12] Like acetic acid,



(7)

pivalic acid allows complexation with the borane. However, the *tert*-butyl group of pivalic acid is bulky enough that it prefers to remain far away from the reaction center. This allows the proper strain-free geometry in the transition state to be attained and results in a rapid protonolysis. It is probable that with the more hindered carboxylic acids, the initial complex is highly sterically strained, driving the equilibrium in eq 7 to the left and thereby causing the protonolysis to be slowed considerably.

Conclusions

It has been determined that a number of alkenyldialkylboranes can be protonolyzed cleanly in high yields utilizing only methanol as the protonolyzing reagent. In those cases where steric hindrance slows the protonolysis, a catalytic amount (1 mol %) of pivalic acid appears to be most effective in bringing about efficient protonolysis. Thus the hydroboration–protonolysis procedure promises to be the method of choice for the efficient, economical synthesis of insect pheromones containing cis double bonds.

Experimental Section

General Comments. The techniques employed extensively during this study are described elsewhere.[13] All glassware was oven-dried at 140 °C for at least 4 h before use, assembled hot, and allowed to cool under a stream of prepurified nitrogen. The transfers of all liquids and solutions were carried out by using oven-dried nitrogen-flushed hypodermic syringes fitted with stainless steel needles. All reactions were carried out under a static pressure of nitrogen.

Materials. THF was distilled under nitrogen from lithium aluminum hydride and then stored under nitrogen in a large ampule with a Teflon stopcock. All alkenyldialkylboranes were prepared according to published procedures.[13] The *B*-alkenyl-9-BBN compounds were distilled materials, while the alkenyldicyclohexyl- and -disiamylboranes were simply used after the volatiles had been removed in vacuo. Reagent grade methanol was deoxygenated,[13] but otherwise used as obtained from J. T. Baker. Triisopropylacetic acid and di-*tert*-butyl acetic acid were kindly provided by Professor M. S. Newman; all other acids were commercial samples and were used as obtained.

Analyses. Gas chromatographic analyses were carried out on a Hewlett-Packard 5750 dual-thermal conductivity chromatograph using a 6 ft × 0.25 in. o.d. column filled with 10% SE-30 on 60/80 AW-DMCS Chromosorb W, using the internal standard technique.

The ^{11}B NMR spectra were recorded on a Varian FT-80A spectrometer operating at 23.267 MHz. The spectra were run on samples in 5-mm tubes held coaxially in 10-mm tubes containing deuteriochloroform lock sample. The spectra were ^{1}H decoupled at 3.5 W.

Protonolysis of Alkenyldialkylboranes. All of the reactions indicated in Table I and II were run as follows: To a dry, nitrogen-flushed, 25-mL flask equipped with a septum inlet and Teflon-coated stirring bar and capped with a condenser was added 5 mmol of the alkenyldialkylborane. Then, 4 mmol of *n*-decane was added, followed by ~2.5 mL of THF. Finally, 5 mmol of the appropriate protonolyzing reagent was added. Those reactions that required heating were heated by a heating mantle at a gentle reflux. Aliquots were taken at various time periods and the appearance of alkene was monitored by GLC analysis. It was previously determined that the alkenyldialkylboranes do not liberate free alkene when injected on the gas chromatograph.

Acknowledgment. We thank Professor Melvin S. Newman of The Ohio State University for samples of triisopropylacetic acid and di-*tert*-butylacetic acid, which were utilized in this study, and to Albany International for their financial support of this work.

(11) Toporcer, L. H.; Dessy, R. E.; Green, S. I. E. *J. Am. Chem. Soc.* **1965**, *87*, 1236.
(12) Toporcer, L. H.; Dessy, R. E.; Green, S. I. E. *Inorg. Chem.* **1965**, *4*, 1649.
(13) Brown. H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975.

Vinylic Organoboranes. 3. Pheromones via Organoboranes. 1. Stereospecific Synthesis of Straight-Chain *Z*-Monoolefinic Insect Pheromones via Lithium (1-Alkynyl)trialkylborates

Herbert C. Brown* and Kung K. Wang[1]

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

Received February 6, 1986

Various insect pheromones with straight-chain *Z*-monoolefinic structures have been prepared from lithium (1-alkynyl)trialkylborates. Treatment of lithium (1-alkynyl)trialkylborates, readily prepared from lithium acetylides and trialkylboranes, with iodine under mild conditions produces the corresponding alkynes in essentially quantitative yield. Monohydroboration of the resultant alkyne with 9-borabicyclo[3.3.1]nonane yields the corresponding (*Z*)-olefin after protonolysis. The combination of these two reaction sequences provides a general route for the synthesis of (*Z*)-olefins. The position of the double bond and the carbon-chain length are easily controlled by properly choosing the initial reactants. The incorporation of functional groups is also easily achieved because of the mild reaction conditions and the tolerance of hydroboration to many functional groups. High yield and purity of the products are obtained.

The study of insect pheromones has recently attracted great attention.[2] This is due to their interesting structures and their potential applications for the control of pest insects.[2a,3] Various synthetic methods have been rapidly

0022-3263/86/1951-4514$01.50/0

developed.

Many insect pheromones, especially those of moths and butterflies, are unsaturated straight-chain aliphatic alcohols, acetates, or aldehydes.[4] For the synthetic materials to be effective attractants in the field, the position, configuration (*E* or *Z*), and number of double bonds as well as the carbon-chain length must be exactly reproduced.[5] The requirement for such high stereospecific synthesis has been a considerable challenge.

The reactions of organoboranes have been shown to be highly stereospecific.[6] It therefore becomes evident that organoboranes will find major application in the synthesis of insect pheromones.[7] As part of a systematic investigation of the synthesis of insect pheromones via organoboranes, we now report a general method for the synthesis of insect pheromones with straight-chain *Z*-monoolefinic structures.

It was previously reported that unsymmetrical alkynes can be readily prepared by the reaction of iodine with (1-alkynyl)trialkylborates in essentially quantitative yield (eq 1–4).[8] Monohydroboration of an alkyne with a borane

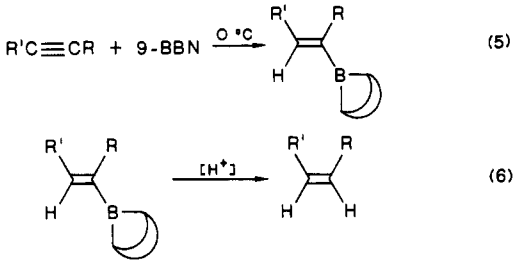
$$HC{\equiv}CR + n\text{-BuLi} \rightarrow LiC{\equiv}CR + n\text{-BuH} \quad (1)$$

$$3\ \text{olefin} + BH_3{\cdot}THF \rightarrow R_3'B \quad (2)$$

$$R_3'B + LiC{\equiv}CR \rightarrow Li^+[R_3'BC{\equiv}CR]^- \quad (3)$$

$$Li^+[R_3'BC{\equiv}CR]^- + I_2 \xrightarrow{-78\ ^\circ C} R'C{\equiv}CR + R_2'BI + LiI \quad (4)$$

reagent, such as 9-borabicyclo[3.3.1]nonane (9-BBN), followed by protonolysis, gave exclusively the corresponding (*Z*)-olefin (eq 5 and 6).[9]



(1) Postdoctoral research associate on Grant 0199-57-13935 from ChemSampCo.

(2) For recent reviews, see: (a) Brand, J. M.; Young, J. C.; Silverstein, R. M. *Fortschr. Chem. Org. Natur.* **1980**, *37*, 1–190. (b) Henrick, C. A. *Tetrahedron* **1977**, *33*, 1845–1889. (c) Rossi, R. *Synthesis* **1977**, 817–836. (d) Rossi, R. *Ibid.* **1978**, 413–434.

(3) Shorey, H. H.; McKelvey, J. J. *Chemical Control of Insect Behavior: Theory and Application*; J. Wiley and Sons: New York, 1977.

(4) Mayer, M. S.; McLaughlin, J. R. *An Annotated Compendium of Insect Sex Pheromones*, Florida Agric. Exp. Station Monograph Series, 1975; no. 6.

(5) (a) Evans, D. A.; Green, C. L. *Chem. Soc. Rev.* **1973**, *2*, 75–97. (b) Eiter, K. *Pure Appl. Chem.* **1975**, *41*, 201–217.

(6) (a) Brown, H. C. *Hydroboration*; W. A. Benjamin: New York, 1962. (b) Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1972. (c) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975. (d) Cragg, G. M. L. *Organoboranes in Organic Synthesis*; Marcel Dekker: New York, 1973.

(7) (a) Negishi, E.; Lew, G.; Yoshida, T. *J. Chem. Soc., Chem. Commun.* **1973**, 874–875. (b) Utimoto, K.; Kitai, M.; Naruse, M.; Nozaki, H. *Tetrahedron Lett.* **1975**, 4233–4234. (c) Negishi, E.; Abramovitch, A. *Ibid.* **1977**, 411–414. (d) Zweifel, G.; Backlund, S. J. *J. Organomet. Chem.* **1978**, *156*, 159–170. (e) Kondo, K.; Murahashi, S.-I. *Tetrahedron Lett.* **1979**, 1237–1240.

(8) Suzuki, A.; Miyaura, N.; Abiko, S.; Itho, M.; Brown, H. C.; Sinclair, J. A.; Midland, M. M. *J. Am. Chem. Soc.* **1973**, *95*, 3080–3081.

(9) (a) Brown, H. C.; Scouten, C. G.; Liotta, R. *J. Am. Chem. Soc.* **1979**, *101*, 96–99. (b) Brown, H. C.; Molander, G. A. *J. Org. Chem.*, previous paper in this issue. (c) Holan, G.; O'Keefe, D. F. *Tetrahedron Lett.* **1973**, 673–674. (d) Leznoff, C. C.; Fyles, T. M. *Can. J. Chem.* **1977**, *55*, 1143–1153. (e) Fyles, T. M.; Leznoff, C. C. *Ibid.* **1977**, *55*, 4135–4143.

Table I. Stereospecific Synthesis of Straight-Chain *Z*-Monoolefinic Insect Pheromones via Lithium (1-Alkynyl)trialkylborates

pheromone	overall isolated yield,[a] % (purity, %)[b]
(*Z*)-9-tricosene	72 (96)
(*Z*)-7-dodecen-1-yl acetate	76 (97)
(*Z*)-7-tetradecen-1-yl acetate	82 (97)
(*Z*)-7-hexadecen-1-yl acetate	78 (97)
(*Z*)-11-hexadecen-1-yl acetate	74 (96)
(*Z*)-7-dodecen-1-ol	95[c] (97)
(*Z*)-11-hexadecen-1-ol	97[c] (96)

[a] Based on alkyne unless otherwise indicated. [b] By GLC. [c] Based on the corresponding acetate.

Therefore, it is apparent that a combination of the above reaction sequences will afford a general method for the synthesis of (*Z*)-olefins. The mild reaction conditions and the tolerance of hydroboration to many functional groups make it especially applicable to the synthesis of insect pheromones.

Results and Discussion

The reaction procedure for the preparation of unsymmetrical alkynes was identical with that described before.[8] The resultant alkynes, without isolation, were hydroborated with 9-BBN at 0 °C to the corresponding *B*-vinyl-9-BBN. Protonolysis with methanol containing 1% of glacial acetic acid gave the corresponding (*Z*)-olefin.[9]

The insect pheromone of the common housefly,[10] (*Z*)-9-tricosene, was prepared from tridecene and 1-decyne. The hydroboration of tridecene with $^1/_3$ equiv of $BH_3{\cdot}THF$ (eq 2) afforded $R_3'B$, where $R_3' = C_{13}H_{27}$.[11] Complex formation of $R_3'B$ with the lithium acetylide derivative of 1-decyne (eq 3), followed by reaction with iodine (eq 4), yielded 9-tricosyne. Monohydroboration of 9-tricosyne with 9-BBN (eq 5), followed by protonolysis (eq 6), produced (*Z*)-9-tricosene.

The overall isolated yield of this essentially one-pot synthesis is 72% (based on 1-decyne). The purity of the product, analyzed by GLC, is 96%. No corresponding *E* isomer was detected by ^{13}C NMR spectroscopy. The previous study also showed that monohydroboration of alkynes with 9-BBN gave only the corresponding (*Z*)-olefins after protonolysis.[11] The experimental results are summarized in Table I.

By properly choosing the initial reactants of alkene and alkyne, various straight-chain *Z*-monoolefinic insect pheromones can be easily prepared. Incorporation of a functional group into the final products can also be achieved.

The insect pheromone of cabbage looper,[12] (*Z*)-7-dodecen-1-yl acetate, was prepared from 5-hexen-1-yl acetate and 1-hexyne. As previous study suggested,[13] $BH_3{\cdot}THF$ reacted only with the double bond of 5-hexen-1-yl acetate to the corresponding $R_3'B$ without attacking the acetate group (eq 7).[11] The presence of the acetate group also did not affect the subsequent reactions (eq 3–6) (Table I).

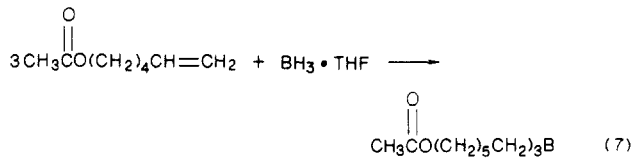
Several other straight-chain *Z*-monoolefinic insect pheromones with acetate functionalities were similarly

(10) Carlson, D. A.; Mayer, M. S.; Sihacek, D. L.; James, J. D.; Beroza, M.; Bierl, B. A. *Science (Washington, D.C.)* **1971**, *174*, 76–78.

(11) Simple 1-alkenes undergo hydroboration with BH_3/THF to place 94% of the boron on the terminal position with 6% at the 2-position. Fortunately, the present study revealed that the rate of iodine induced migration (eq 4) of the terminal alkyl group was faster than the secondary alkyl group in this case.

(12) Berger, R. S. *Ann. Entomol. Soc. Am.* **1966**, *59*, 767–771.

(13) Dulou, R.; Chrétien-Bessière, Y. *Bull. Soc. Chim. Fr.* **1959**, 1362–1365.



$$3CH_3CO(CH_2)_4CH{=}CH_2 + BH_3 \cdot THF \longrightarrow (CH_3CO(CH_2)_5CH_2)_3B \quad (7)$$

prepared. The carbon-chain length and the position of the double bond were easily controlled. (*Z*)-7-Tetradecen-1-yl acetate[14] and (*Z*)-7-hexadecen-1-yl acetate[14,15] were prepared by choosing 1-octyne and 1-decyne as the initial alkyne, respectively (eq 1). (*Z*)-11-Hexadecen-1-yl acetate[14,16] was prepared from 9-decen-1-yl acetate and 1-hexyne. The overall isolated yields and the purities of the products are uniformly high (Table I).

(*Z*)-7-Dodecen-1-ol[17] and (*Z*)-11-hexadecen-1-ol[16b,c] were obtained by hydrolyzing the corresponding acetates with base. The experimental results are also summarized in Table I.

The results summarized in Table I clearly establish that the present reaction procedure is a general method for the synthesis of insect pheromones with a straight-chain *Z*-monoolefinic structure. To further enhance its utility and to avoid the loss of two alkyl groups of $R_3'B$ (eq 4), research is now directed to find a suitable disubstituted borane, such as catecholborane,[6] instead of BH_3·THF as the hydroborating agent (eq 2).

Conclusion

Since the discovery of the hydroboration reaction,[18] the chemistry of organoboranes has been rapidly developed. Many fascinating characteristics have been discovered and applied to natural product synthesis.[19] The present study provides an example for a promising application of organoboranes in the synthesis of insect pheromones. A systematic investigation is being undertaken to explore the full potentiality of organoboranes in the synthesis of insect pheromones.

Experimental Section

General Comments. General procedures for the manipulation of boron reagents have been outlined in Chapter 9 of ref 6c. All glassware, syringes, and needles were oven-dried at 140 °C for several hours. The glassware was assembled while hot and cooled under a stream of dry nitrogen. Syringes were assembled and fitted with needles while hot and then cooled as assembled units. They were flushed with nitrogen immediately before use. All reactions were carried out under nitrogen until the oxidation stage. GLC analysis of the products was studied on a Varian 1200 gas chromatograph on a 6 ft ×1/8 in. 5% SE-30 column. ^1H and ^{13}C NMR spectra were taken on Varian T-60 and FT-80A spectrometers, respectively, using $CDCl_3$ as solvent and Me_4Si as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 137 sodium chloride spectrophotometer. High resolution mass spectra were recorded on a CEC 21-110B mass spectrometer.

Materials. The starting alkenes and alkynes were purchased from Chemical Samples Co. The alkynes were distilled from sodium borohydride prior to use. THF was distilled from lithium aluminum hydride under nitrogen. BH_3·THF and 9-BBN in THF solvent were prepared and standardized as reported previously.[6c] *n*-Butyllithium in hexane solution was obtained from Ventron Co. Reagent grade iodine (Mallinckrodt) was used. The silica gel used was 40–63 μm (230–400 mesh) silica gel 60 (E. Merck No. 9385).

(*Z*)-9-Tricosene. A dry, 500-mL flask equipped with a magnetic stirring bar and septum inlet was flushed with nitrogen. The flask was charged under nitrogen with 16.4 g (90.0 mmol) of 1-tridecene and 30 mL of dry THF via syringe. The flask is immersed in an ice-bath, and 15.6 mL (30.0 mmol) of 1.93 *M* borane/THF complex was added dropwise to the stirred solution. The solution was then stirred at room temperature for 1 h and cooled to 0 °C. In another dry, nitrogen-flushed 100-mL flask equipped with a magnetic stirring bar and septum inlet were placed 30 mL of THF and 4.15 g (30.0 mmol) of 1-decyne. The flask was cooled in an ice bath and 13.8 mL (30.0 mmol) of a 2.17 M solution of *n*-butyllithium in hexane was added to form the corresponding lithium acetylide. The lithium acetylide solution was then transferred into the 500-mL flask. The reaction flask was added with an additional 100 mL of THF and cooled to −78 °C. The entire reaction solution solidified. A solution of 7.61 g (30.0 mmol) of iodine in 30 mL of THF was added dropwise through a Teflon double-ended needle. The reaction flask was shaken vigorously during the addition. After an additional 45 min at −78 °C, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The reaction flask was then cooled to 0 °C and 61.2 mL (34.5 mmol, 15% excess) of a 0.564 M solution of 9-BBN in THF was added. The reaction mixture was kept at 0 °C for 48 h. The resultant *B*-vinyl-9-BBN adduct was then protonolyzed with 6 mL of methanol containing about 1% of glacial acetic acid at 25 °C for 1 h. The solution was then treated wth 24 mL of 3 N aqueous sodium hydroxide followed by the dropwise addition of 24 mL of 30% hydrogen peroxide at 0 °C to oxidize the borane byproducts. Pentane, 300 mL, was added and the solution was washed twice with 300 mL of water containing 0.5 g of sodium thiosulfate to remove the residual iodine. The organic layer was separated and the solvent was removed on a Rotovac. The low-boiling impurities were distilled off under high vacuum (10^{-3} mmHg). The product was then purified on a short silica gel column (5 cm in length and 4 cm in diameter). Pentane, 1000 mL, was chosen to elute the column. A final 100 mL of pentane containing 5% of ethyl acetate was used to elute the last fraction. The eluant was collected every 100 mL and analyzed by GLC. The solvent of the combined eluant was removed on a Rotovac. A colorless liquid of 6.97 g (72% based on 1-decyne) of (*Z*)-9-tricosene was obtained. The purity of the product was found to be 96% by GLC. No corresponding *E* isomer was detected by ^{13}C NMR spectroscopy. The physical and spectral data are as follows: n^{20}_D 1.4522 [lit.[20] n^{23}_D 1.4532]; IR (neat) 1665 (w), 1470 (s), 1390 (m) cm^{-1}; ^1H NMR δ 0.60–2.30 (m, 44 H), 5.36 (t, 2 H, J = 4.6 Hz); ^{13}C NMR δ 14.2, 22.9, 27.4, 29.6, 29.9, 32.2, 129.9; high resolution mass spectrum, m/e 322.360 ($M^{+\cdot}$) ($C_{23}H_{46}$ requires 322.359).

(*Z*)-7-Dodecen-1-yl Acetate. The same reaction procedure was used as described above except the complex formation between $R_3'B$ and lithium acetylide (eq 3) was carried out at −78 °C. 5-Hexen-1-yl acetate and 1-hexyne were the initial reactants. 5-Hexen-1-yl acetate was prepared from 5-hexen-1-ol by adding 100 mL of pyridine and 100 mL of acetic anhydride to 25.1 g (250 mmol) of 5-hexen-1-ol and stirring at room temperature overnight. The reaction mixture was treated with 300 mL of water and extracted twice with 100 mL of diethyl ether. The organic layer was washed twice with 500 mL of 10% aqueous hydrogen chloride solution and twice with 200 mL of saturated aqueous sodium chloride solution. The organic phase was dried over anhydrous magnesium sulfate. Distillation of the product yielded 30.1 g (85%) of 5-hexen-1-yl acetate (bp 68–70 °C, 14 mm). The overall isolated yield of (*Z*)-7-dodecen-1-yl acetate was 5.16 g (76% based on 1-hexyne). The purity of the product was found to be 97% by GLC. No corresponding *E* isomer was detected by ^{13}C NMR spectroscopy. The physical and spectral data are as follows: n^{20}_D

(14) Roelofs, W. L.; Comeau, A. *J. Econ. Entomol.* **1973**, *63*, 969–974.
(15) (a) Keller, J. C.; Sheets, L. W.; Green, N.; Jacobson, M. *J. Econ. Entomol.* **1969**, *62*, 1520–1521. (b) Green, N.; Jacobson, M.; Keller, J. C. *Experientia* **1969**, *25*, 682–683.
(16) (a) Chisholm, M. D.; Steck, W. F.; Arthur, A. P.; Underhill, E. W. *Can. Entomol.* **1975**, *107*, 361–366. (b) Struble, D. L.; Swailes, G. E. *Environ. Entomol.* **1975**, *4*, 632–636. (c) Underhill, E. W.; Steck, W. F.; Chisholm, M. D. *Ibid.* **1976**, *5*, 307–310.
(17) Weatherston, J.; Davidson, L. M.; Simonins, D. *Can. Entomol.* **1974**, *106*, 781–782.
(18) (a) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1956**, *78*, 5694–5695. (b) Brown, H. C.; Subba Rao, B. C. *Ibid* **1959**, *81*, 6428–6434.
(19) (a) Partridge, J. J.; Chadha, N. K.; Uskoković, M. R. *J. Am. Chem. Soc.* **1973**, *95*, 532–540. (b) Partridge, J. J.; Chadha, N. K.; Uskoković, M. R. *Ibid.* **1973**, *95*, 7171–7172. (c) Evans, D. A.; Crawford, T. C.; Thomas, R. C.; Walker, J. A. *J. Org. Chem.* **1976**, *41*, 3947–3953.
(20) Cargill, R. L.; Rosenblum, M. G. *J. Org. Chem.* **1972**, *37*, 3971.

1.4418 [lit.[21] n^{25}_D 1.4420]; IR (neat) 1745 (s), 1665 (w), 1470 (m), 1375 (m), 1240 (s), 1045 (m); ^{1}H NMR δ 0.60–1.80 (m, 15 H), 1.80–2.30 (m, 7 H; CH_3CO_2 s, at 2.00), 4.05 (t, 2 H, J = 6.0 Hz), 5.35 (t, 2 H, J = 4.6 Hz); ^{13}C NMR δ 14.0, 20.8, 22.5, 26.1, 27.1, 27.3, 28.9, 29.1, 29.8, 32.2, 64.5, 129.7, 130.1, 170.5; high resolution mass spectrum, m/e 226.194 ($M^{+\bullet}$) ($C_{14}H_{26}O_2$ requires 226.193).

(Z)-7-Tetradecen-1-yl Acetate. 1-Octyne was used as the initial alkyne. The overall isolated yield was 6.26 g (82% based on 1-octyne). The purity of the product as analyzed by GLC was 97%. No corresponding E isomer was detected by ^{13}C NMR spectroscopy. The physical and spectral data are as follows: n^{20}_D 1.4478 [lit.[22] n^{20}_D 1.4486]; IR (neat) 1745 (s), 1665 (w), 1470 (m), 1375 (m), 1240 (s), 1045 (m) cm^{-1}; ^{1}H NMR δ 0.60–1.80 (m, 19 H), 1.80–2.30 (m, 7 H; CH_3CO_2 s, at 2.00), 4.05 (t, 2 H, J = 6.0 Hz), 5.35 (t, 2 H, J = 4.6 Hz); ^{13}C NMR δ 14.1, 20.7, 22.8, 26.1, 27.3, 27.4, 28.9, 29.1, 29.9, 30.0, 32.0, 64.4, 129.7, 130.1, 170.3; high resolution mass spectrum, m/e 254.225 ($M^{+\bullet}$) ($C_{16}H_{30}O_2$ requires 254.224).

(Z)-7-Hexadecen-1-yl Acetate. 1-Decyne was used as the initial alkyne. The overall isolated yield was 6.57 g (78% based on 1-decyne). The purity, as analyzed by GLC, was 97%. No corresponding E isomer was detected by ^{13}C NMR spectroscopy. The physical and spectral data are as follows: n^{20}_D 1.4496 [lit.[15b] n^{25}_D 1.4484]; IR (neat) 1745 (s), 1665 (w), 1470 (m), 1375 (m), 1240 (s), 1045 (m) cm^{-1}; ^{1}H NMR δ 0.60–1.80 (m, 23 H), 1.80–2.30 (m, 7 H; CH_3CO_2 s at 2.00), 4.05 (t, 2 H, J = 6.0 Hz), 5.35 (t, 2 H, J = 4.6 Hz); ^{13}C NMR δ 14.1, 20.7, 22.8, 26.1, 27.3, 27.4, 28.9, 29.1, 29.5, 29.8, 30.0, 32.1, 64.4, 129.6, 130.1, 170.4; high resolution mass spectrum, m/e 282.252 ($M^{+\bullet}$) ($C_{18}H_{34}O_2$ requires 282.255).

(Z)-11-Hexadecen-1-yl Acetate. 9-Decen-1-yl acetate and 1-hexyne were the initial reactants. 9-Decen-1-yl acetate was prepared from 9-decen-1-ol by a method similar to that used in the synthesis of 5-hexen-1-yl acetate. The overall isolated yield of (Z)-11-hexadecen-1-yl acetate was 6.24 g (74% based on 1-hexyne). The purity, as analyzed by GLC, was 96%. No E isomer was detected by ^{13}C NMR spectroscopy. The physical and spectral data are as follows: n^{20}_D 1.4498; IR (neat) 1745 (s), 1665 (w), 1470 (m), 1375 (m), 1240 (s), 1045 (m) cm^{-1}; ^{1}H NMR δ 0.60–1.80 (m, 23 H), 1.80–2.30 (m, 7 H; CH_3CO_2 s at 2.00), 4.05 (t, 2 H, J = 6.0 Hz), 5.35 (t, 2 H, J = 4.6 Hz); ^{13}C NMR δ 14.0, 20.7, 22.5, 26.1, 27.1, 27.4, 28.9, 29.5, 29.7, 29.9, 32.2, 64.5, 129.9, 170.5; high resolution mass spectrum, m/e 282.255 ($M^{+\bullet}$) ($C_{18}H_{34}O_2$ requires 282.255).

(Z)-7-Dodecen-1-ol. A 250-mL flask, equipped with a condenser and a magnetic stirring bar, was charged with 3.40 g (15.0 mmol) of (Z)-7-dodecen-1-yl acetate, 50 mL of 10% aqueous sodium hydroxide solution, and 50 mL of ethanol. The reaction mixture was heated to reflux for 1 h to hydrolyze the acetate. Pentane, 150 mL, was then added to the reaction flask. The organic layer was separated and washed twice with 100 mL of water. The solvent was removed on a Rotovac. A colorless liquid of 2.63 g (95%) of (Z)-7-dodecen-1-ol was obtained. GLC analysis showed the product to be 97% pure. The physical and spectral data are as follows: n^{20}_D 1.4540 [lit.[22] n^{20}_D 1.4554); IR (neat) 3300 (s), 1665 (w), 1470 (s), 1060 (s) cm^{-1}; ^{1}H NMR δ 0.60–1.80 (m, 15 H), 1.80–2.35 (m, 4 H), 2.40–2.75 (br, 1 H, OH), 3.40–3.80 (br, 2 H), 5.35 (t, 2 H, J = 4.6 Hz); ^{13}C NMR δ 14.0, 22.4, 25.9, 27.0, 27.3, 29.2, 29.9, 32.1, 32.9, 62.8, 129.8, 130.1; high resolution mass spectrum, m/e 184.190 ($M^{+\bullet}$) ($C_{12}H_{24}O$ requires 184.182).

(Z)-11-Hexadecen-1-ol. The same reaction product was used to hydrolyze 4.24 g (15.0 mmol) of (Z)-11-hexadecen-1-yl acetate as described above. A colorless liquid of 3.48 g (97%) of (Z)-11-hexadecen-1-old was obtained. GLC analysis showed the product to be 96% pure. The physical and spectral data are as follows: n^{20}_D 1.4578; IR (neat) 3300 (m), 1665 (w), 1470 (m), 1060 (m) cm^{-1}; ^{1}H NMR δ 0.60–1.80 (m, 23 H), 1.80–2.35 (m, 4 H), 2.85–3.10 (br, 1 H, OH), 3.40–3.80 (br, 2 H), 5.35 (t, 2 H, J = 4.6 Hz); ^{13}C NMR δ 14.0, 22.5, 26.0, 27.0, 27.3, 29.5, 29.8, 32.2, 32.9, 62.7, 129.9; high resolution mass spectrum, m/e 240.245 ($M^{+\bullet}$) ($C_{16}H_{32}O$ requires 240.245).

Acknowledgment. We thank Chemical Samples Co. for support of this work.

Registry No. 1-tridecene, 2437-56-1; 1-decyne, 764-93-2; 1-lithiodecyne, 21433-46-5; (Z)-9-tricosene, 27519-02-4; 5-hexen-1-yl acetate, 5048-26-0; 1-hexyne, 693-02-7; 5-hexen-1-ol, 821-41-0; (Z)-7-dodecen-1-yl acetate, 14959-86-5; 1-octyne, 629-05-0; (Z)-7-tetradecen-1-yl acetate, 16974-10-0; (Z)-7-hexadecen-1-yl acetate, 23192-42-9; 9-decen-1-yl acetate, 50816-18-7; 9-decen-1-ol, 13019-22-2; (Z)-11-hexadecen-1-yl acetate, 34010-21-4; (Z)-7-dodecen-1-ol, 20056-92-2; (Z)-11-hexadecen-1-ol, 56683-54-6.

(21) Green, N.; Jacobson, M.; Henneberry, J. J.; Kishaba, A. N. *J. Med. Chem.* **1967**, *10*, 533–535.

(22) Kovaleva, A. S.; Bulina, V. M.; Ivanov, L. L.; Pyatnova, Yu. B.; Evstigneeva, R. P. *J. Org. Chem. USSR Engl. Trans.* **1974**, *10*, 700–704.