Preparation of (Z)-Alkenes, Ketones, and Alkynes via Trialkyltin Chloride Induced Intramolecular Transfer Reaction of Lithium 1-Alkynyltrialkylborates. Stereoselective Synthesis of the Sex Pheromones of the Douglas Fir Tussock Moth, the Gypsy Moth, and the Wild Silkmoth *Antheraea polyphemus*

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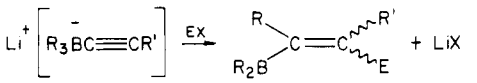
Trialkyltin chloride was used to induce selective migration of a primary alkyl group from the boron atom to the adjacent acetylenic carbon atom of lithium 1-alkynyltrialkylborate complexes derived from *B*-alkyl-9-borabicyclo[3.3.1]nonanes and 1-lithio-1-alkynes. Protonolysis of the resultant olefinic intermediate substituted with boron and tin functionalities on the adjacent vinyl carbon atoms provided the corresponding (*Z*)-alkene. Oxidation or iodination afforded the corresponding ketone or alkyne, respectively. The high selectivity of 9-borabicyclo[3.3.1]nonane as a hydroborating agent toward the terminal double bond allowed easy incorporation of internal double bond and triple bond into the alkyl group of the starting *B*-alkyl-9-borabicyclo[3.3.1]nonane. Various types of diene, enyne, enone, ynone, and diyne were thus synthesized. These reactions were also successfully adopted for the stereoselective synthesis of the sex pheromones of the Douglas fir tussock moth, the gypsy moth, and the wild silkmoth *Antheraea polyphemus*.

The intramolecular-transfer reactions of lithium 1-alkynyltrialkylborate induced by various types of electrophiles have found many applications in the construction of carbon–carbon bonds.[1]



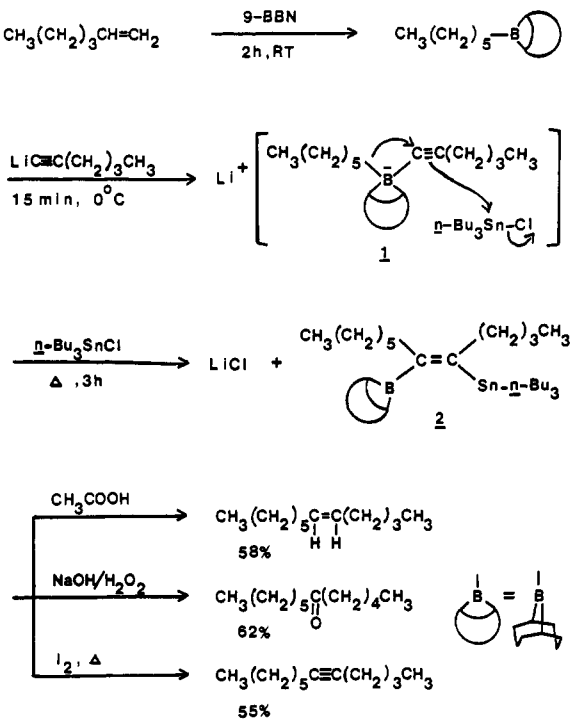
EX = *n*-Bu_3SnCl, Me_3SiCl, CH_3CH_2COOH, etc

The stereoselective migration of a primary alkyl group from the boron atom to the adjacent acetylenic carbon atom to form the corresponding olefin with the migrating alkyl group *trans* to the electrophile was achieved by using tri-*n*-butyltin chloride as the inducing agent.[2] Protonolysis or oxidation of the olefinic intermediate provided the corresponding (*Z*)-alkene or ketone, respectively. However, only one of the three alkyl groups on the boron atom was utilized. This inefficiency could be circumvented by using a dialkylborane as the hydroborating agent to react with an olefin to form the starting trialkylborane.[3] The two alkyl groups on the dialkylborane could serve as "blocking" groups if they do not compete in the subsequent migration step. This could prevent the loss of valuable starting olefins. Moreover, the use of a dialkylborane as the hydroborating agent will provide one more advantage over that of BH_3·THF complex. It has been clearly established that certain dialkylboranes are much more reactive toward the terminal double bond than toward the internal double bond and triple bond.[4] Consequently, one could selectively hydroborate a terminal double bond in the presence of an internal double bond or triple bond and allow these unsaturations to be carried over through the reaction sequences to the final products. This selectivity could not be achieved with BH_3·THF complex as the hydroborating agent.[4c]

Results and Discussion

In searching for such a dialkylborane as the hydroborating agent, 9-borabicyclo[3.3.1]nonane (9-BBN) was found to provide good blocking groups as well as show high selectivity toward the terminal double bond.[4a,b] The reaction sequences for the syntheses of (*Z*)-5-dodecene, 6-dodecanone, and 5-dodecyne are outlined in Scheme I. Tri-*n*-butyltin chloride was used to induce the intramolecular-transfer reaction of the organoborate "ate" complex **1**. The reaction mixture in THF was refluxed for 3 h. The refluxing was necessary to rearrange the initially formed undesired addut due to the migration of the cyclooctyl ring to the desired adduct **2** derived from the migration of the *n*-hexyl group. This rearrangement phenomenon has also been observed previously for a similar intermediate.[5] Protonlysis of **2** with glacial acetic acid provided (*Z*)-5-dodecene in 58% isolated yield with exceptionally high stereoselectivity (>98% *Z*). Oxidation or iodination of **2**

Scheme I



(1) Negishi, E. *J. Organomet. Chem.* **1976**, *108*, 281–324.
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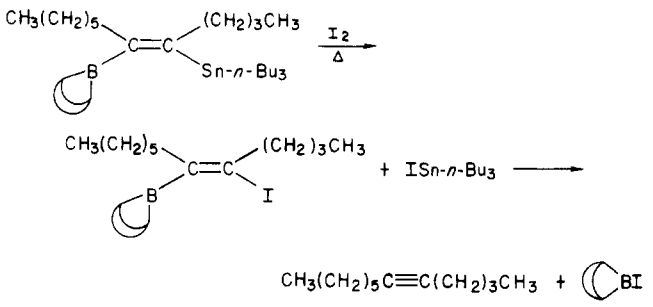
Table I. Synthesis of (*Z*)-Alkenes, Ketones, and Alkynes via Lithium 1-Alkynyltrialkylborates

entry	alkene for *B*-R-9-BBN	alkyne	reactant	product[a]	isolated yield, %
1	1-hexene	1-hexyne	HOAc	(*Z*)-5-dodecene	58
2	1-decen-4-yne	1-undecyne		(*Z*)-11-heneicosen-6-yne	68
3	5-methyl-1-hexene	1-dodecyne		(*Z*)-2-methyl-7-octadecene[b]	66
4	(*E*)-6,9-decadien-1-yl acetate	1-hexyne		(6*E*,11*Z*)-6,11-hexadecadien-1-yl acetate[c]	52
5	1-hexene	1-hexyne	$NaOH/H_2O_2$	6-dodecanone	62
6	1-decen-4-yne	1-undecyne		6-heneicosyn-11-one	58
7	(*Z*)-1,4-decadiene	1-undecyne		(*Z*)-6-heneicosen-11-one[c,d]	54
8	(*E*)-1,4-decadiene	1-undecyne		(*E*)-6-heneicosen-11-one[c,d]	55
9	1-hexene	1-hexyne	I_2	5-dodecyne	55
10	4-vinylcyclohexene	1-hexyne		1-(3-cyclohexenyl)-3-octyne	64
11	styrene	1-hexyne		1-phenyl-3-octyne	62
12	(*E*)-1,4-decadiene	1-hexyne		(*E*)-10-hexadecen-5-yne[c]	57
13	1-decen-4-yne	1-hexyne		5,10-hexadecadiyne	50
14	2-methyl-1-pentene	1-hexyne		8-methyl-5-undecyne	40

[a] Isolated pure materials (>97% by GLC) by vacuum distillation of 30 mmol reactions with tri-*n*-butyltin chloride as the inducing electrophile unless otherwise indicated. [b] The product contained ca. 10% of bis(tri-*n*-butyltin) oxide. This byproduct was removed in the following epoxidation step. [c] 10 mmol reaction. [d] Trimethyltin chloride was used as the inducing electrophile.

afforded 6-dodecanone or 5-dodecyne, respectively. The iodination reaction for the formation of 5-dodecyne presumably proceeded through the replacement of the tri-*n*-butyltin substituent with iodine[6] followed by a facile elimination of *B*-iodo-9-BBN.[7] Direct treatment of **1** with

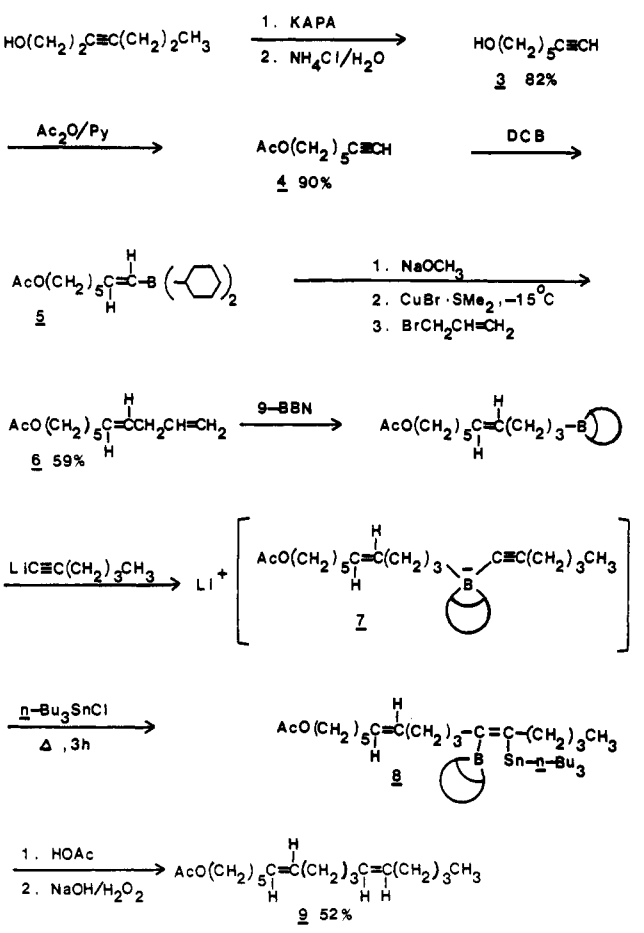


iodine would result in an irreversible migration of the cyclooctyl ring.[8] By incorporating an internal double bond or triple bond into the starting terminal olefins, various types of diene, enyne, enone, ynone, and diyne have also been prepared (Table I).

Synthesis of Sex Pheromones

The reaction sequences outlined in Scheme I have been successfully adopted for the synthesis of the sex pheromones of the Douglas fir tussock moth, the gypsy moth, and the wild silkmoth *Antheraea polyphemus*.[9] (*Z*)-6-Heneicosen-11-one (entry 7) has been identified as the sex attractant of the Douglas fir tussock moth.[10] Its corresponding *E* isomer was also synthesized (entry 8). Epoxidation of (*Z*)-2-methyl-7-octadecene (entry 3) with *m*-chloroperbenzoic acid provided the racemic (*Z*)-7,8-epoxy-2-methyloctadecane (disparlure) in 78% isolated yield. The optically active (7*R*,8*S*)-(+)-disparlure has been identified as the sex attractant emitted by the female gypsy moth (*Porthetria dispar* L.).[11] The reaction sequence for the synthesis of the major component of the sex attractant of the wild silkmoth *Antheraea polyphemus*, (6*E*,11*Z*)-6,11-hexadecadien-1-yl acetate (entry 4),[12] is outlined in Scheme II.

Scheme II



The isomerization of 3-heptyn-1-ol to 6-heptyn-1-ol (**3**) was carried out with potassium 3-aminopropylamide (KAPA).[13] The alcohol **3** was then converted to the corresponding acetate **4**. The terminal triple bond of the acetate was then hydroborated with dicyclohexylborane (DCB) to form the corresponding *trans*-alkenyldicyclohexylborane **5**. Cross-coupling of the alkenyl group in **5**

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with allyl bromide to form (E)-1,4-diene **6** was achieved by using the copper-promoted coupling reaction described previously.[14] Selective hydroboration of the terminal double bond in **6** with 9-BBN followed by the treatment with 1-lithio-1-hexyne provided the borate complex **7**. Intramolecular migration induced by tri-*n*-butyltin chloride gave **8**, which upon protonolysis afforded (6*E*,11*Z*)-6,11-hexadecadien-1-yl acetate **9** in 52% isolated yield. The overall yield from 3-heptyn-1-ol was 23%.

The ^{13}C NMR spectrum of **9** showed only four peaks for the vinyl carbon atoms (δ 129.57, 130.12, 130.24, and 130.48), indicating the absence of the other three geometric isomers. The configuration of the trans double bond in **9** was determined by the hydroboration of the triple bond in **4** with dicyclohexylborane followed by the retention of the trans configuration in the cross-coupling reaction with allyl bromide. The configuration of the cis double bond was determined by the stereoselective intramolecular rearrangement of the organoborate complex **7**.

In summary, the high chemo- and regioselectivity of 9-BBN as a hydroborating agent coupled with the high stereoselectivity of trialkyltin chloride induced rearrangement of lithium 1-alkynyltrialkylborates provides an efficient method for the synthesis of various types of (Z)-alkenes, ketones, and alkynes. The olefinic intermediates **2** constructed with two reactive sites are being explored for other valuable chemical transformations.

Experimental Section

General procedures described in Chapter 9 of ref 3 for the manipulation of organoborane and other organometallic reagents were employed. All glassware, syringes, and needles were oven dried at 140 °C for several hours. The glassware were assembled while hot and cooled under a stream of dry nitrogen. GLC analyses were performed on a Varian 1440 gas chromatograph equipped with a 3 ft × 0.125 in. column packed with 10% SP-2100 on 100/120 Supelcoport. ^1H and ^{13}C NMR spectra were recorded on a Varian EM-360 (60 MHz in ^1H) and a Varian CFT-20 (20 MHz in ^{13}C) NMR spectrometer, respectively ($CDCl_3$, Me_4Si). IR spectra were taken on a Beckman IR 8 spectrometer. Mass spectra were obtained on a Finnigan 4021 GC/MS instrument. Elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, TN.

Materials. Tetrahydrofuran was distilled from $LiAlH_4$ and stored under nitrogen. 9-Borabicyclo[3.3.1]nonane was prepared as described previously.[15] Straight-chain terminal olefins, *m*-chloroperbenzoic acid, 1,3-diaminopropane, potassium hydride (35% in oil), tri-*n*-butyltin chloride, and trimethyltin chloride were obtained from Aldrich Chemical Co. and used directly without further purification. 5-Methyl-1-hexene was purchased from Tridom Chemical Inc. and used as received. Alkynes were obtained from Farchan Laboratories. *n*-Butyllithium in hexane was obtained from Alfa and used after the concentration was standardized. (E)-1,4-Decadiene,[14] (Z)-1,4-decadiene,[16] and 1-decen-4-yne[17] were prepared according to the procedures described previously.

Preparation of (Z)-Alkenes. The following procedure for the preparation of (Z)-5-dodecene is representative. To an oven-dried, nitrogen-flushed 250-mL round-bottomed flask equipped with a refluxing condenser and a magnetic stirring bar was successively added via syringe 20 mL of THF and 3.74 mL of 1-hexene (2.52 g, 30 mmol). To the mixture was then added 55.6 mL of 0.54 M 9-BBN solution in THF (30 mmol) followed by stirring at room temperature for 2 h before cooling to 0 °C. In a separate 50-mL Erlenmeyer flask, 30 mmol of 1-lithio-1-hexyne was prepared by adding dropwise 12.7 mL of *n*-butyllithium (2.37 M in hexane, 30 mmol) to 3.45 mL of 1-hexyne (2.47 g, 30 mmol) in 20 mL of THF at 0 °C. After 15 min, 1-lithio-1-hexyne was added slowly through a stainless steel double-ended needle into the round-bottomed flask. The reaction mixture was allowed to warm to room temperature for 15 min and then 8.95 mL of tri-*n*-butyltin chloride (10.74 g, 33 mmol) was added. The reaction mixture was then heated to reflux for 3 h. After cooling to 0 °C, 5.4 mL of glacial acetic acid was introduced. The reaction mixture was refluxed again for 1 h to ensure complete protonolysis. The usual oxidative workup with 30 mL of methanol, 30 mL of 3 N NaOH, and 12 mL of 30% H_2O_2 was used to remove the boron byproducts. The organic layer was then separated and washed three times each with 75 mL of water and 75 mL of 6 N NaOH to remove 1,5-cyclooctanediol and some low boiling organotin compounds. After removing of solvent, the residue was column chromatographed on aluminum oxide with hexane as eluent. Distillation on a short-path distilling head afforded 2.94 g (58% yield) of (Z)-5-dodecene as a colorless liquid: bp 36 °C (0.4 torr); n^{20}_D 1.4342; IR (neat) 3020 (s), 1655 (w), 1460 (s), 1380 (m), 720 (m) cm^{-1}; ^1H NMR δ 0.90 (br, 6 H), 1.0–1.5 (br, 12 H), 1.7–2.2 (br, 4 H), 5.4 (t, 2 H); ^{13}C NMR δ 14.08, 22.55, 22.90, 27.13, 27.44, 29.26, 30.00, 32.07, 32.25, 129.95. GLC analysis showed that the product had a chemical purity of >97%. The presence of only a single vinyl carbon peak at 129.95 δ indicated the absence of any significant amount of the corresponding *E* isomer (<2%). The E isomer has a vinyl carbon peak at 130.5 δ and could be clearly identified.

(Z)-11-Heneicosen-6-yne: bp 130 °C (7×10^{-2} torr); n^{20}_D 1.4643; IR (neat) 3020 (w), 1460 (m), 715 (w) cm^{-1}; ^1H NMR δ 0.9 (br, 6 H), 1.3 (br, 22 H), 2.2 (br, 8 H), 5.45 (t, 2 H); ^{13}C NMR δ 14.12, 18.43, 18.92, 22.46, 22.89, 26.48, 27.46, 29.17, 29.43, 29.60, 29.88, 30.02, 31.32, 32.17, 79.83, 80.26, 128.85, 130.85; mass spectrum, *m/e* 290 (parent ion). Anal. Calcd for $C_{21}H_{38}$: C, 86.82; H, 13.18. Found: C, 86.75; H, 12.92.

(Z)-2-Methyl-7-octadecene:[18] bp 96 °C (5×10^{-3} torr) [lit.[18b] bp 100–102 °C (5×10^{-2} torr)]; n^{20}_D 1.4542 (lit.[18b] n^{20}_D 1.4449); IR (neat) 3020 (w), 1465 (w) cm^{-1}; ^1H NMR δ 0.9 (m, 9 H), 1.0–1.6 (br, 23 H), 1.7–2.2 (br, 4 H), 5.4 (t, 2 H); ^{13}C NMR δ 14.15, 22.71, 22.82, 27.23, 27.34, 28.08, 29.49, 29.82, 30.16, 32.09, 39.07, 129.89. The product contained ca. 10% of bis(tri-*n*-butyltin) oxide as indicated by GLC and ^{13}C NMR spectrum. This byproduct was removed in the following epoxidation step for the synthesis of the sex pheromone of the gypsy moth.

(Z)-7,8-Epoxy-2-methyloctadecane (Disparlure).[18] Treatment of (Z)-2-methyl-7-octadecene (2.66 g, 10 mmol) with *m*-chloroperbenzoic acid according to the procedure described previously[19] provided 2.21 g (78% yield) of (±)-disparlure as a colorless liquid: bp 108 °C (5×10^{-3} torr) [lit.[18b] bp 117–118 °C (5×10^{-2} torr)]; n^{20}_D 1.4471 (lit.[18b] n^{20}_D 1.4460); IR (neat) 1470 (s), 1390 (m), 1370 (m) cm^{-1}; ^1H NMR δ 0.7–1.0 (m, 9 H), 1.1–1.7 (m, 27 H), 2.7–3.0 (m, 2 H); ^{13}C NMR δ 14.15, 22.68, 26.73, 27.02, 27.44, 28.00, 29.47, 29.69, 32.03, 39.05, 57.12; chemical purity >99% by GLC.

(6E,11Z)-6,11-Hexadecadien-1-yl Acetate.[20] 3-Heptyn-1-ol was isomerized to 6-heptyn-1-ol via the acetylene "zipper" reaction as described previously.[13] The reaction was carried out by adding 6.16 mL of 3-heptyn-1-ol (5.6 g, 50 mmol) to a 500-mL reaction flask containing 150 mmol of potassium 3-aminopropylamide in 150 mL of 1,3-diaminopropane at 0 °C. After stirring at room temperature for 4 h, the reaction mixture was then transferred dropwise via a stainless steel double-ended needle to a 500-mL Erlenmeyer flask containing 100 mL of saturated aqueous ammonium chloride and 50 mL of ether maintained at 0 °C. The ether layer was separated, washed with water, and then dried over magnesium sulfate. Distillation afforded 4.57 g (82% yield) of 6-heptyn-1-ol as a colorless liquid (bp 102 °C (ca. 25 torr)). 6-Heptyn-1-ol (4.48 g, 40 mmol) was then treated with acetic anhydride and pyridine to form the corresponding acetate in 90%

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isolated yield (5.26 g, bp 110 °C (ca. 25 torr)). 6-Heptyn-1-yl acetate (2.31 g, 15 mmol) was converted to (6*E*)-6,9-decadien-1-yl acetate (1.74 g, 59% isolated yield) according to the procedure described previously.[14] The product had the following: bp 49 °C (5×10^{-3} torr); n^{20}_D 1.4519; IR (neat), 1745 (s), 1645 (w), 1365 (m), 1240 (s), 1040 (m), 995 (w), 970 (m), 910 (m) cm^{-1}; ^1H NMR δ 1.0–2.2 (br, 8 H), 2.0 (s, 3 H), 2.7 (br, 2 H), 4.05 (t, 2 H), 4.8–6.2 (m, 5 H); ^{13}C NMR δ 20.87, 25.45, 28.56, 29.11, 32.41, 36.75, 64.45, 114.80, 127.98, 131.28, 137.32, 170.89. (6*E*)-6,9-Decadien-1-yl acetate (1.96 g, 10 mmol) was then converted to (6*E*,11*Z*)-6,11-hexadecadien-1-yl acetate (1.46 g, 52% yield) as shown in Scheme II. Protonolysis with 1.14 mL of glacial acetic acid was carried out at refluxing temperature for 1 h. The usual oxidative workup with $NaOH/H_2O_2$ was carried out at 0 °C followed by warming to room temperature to avoid ester hydrolysis. The product had the following: bp 106 °C (5×10^{-3} torr) [lit.[20a] bp 120–130 °C (1×10^{-2} torr)]; n^{20}_D 1.4631; IR (neat) 1740 (s), 1460 (m), 1365 (m), 1235 (s), 1040 (m), 965 (m), 720 (w) cm^{-1}; ^1H NMR δ 0.9 (br, 3 H), 1.0–2.2 (br, 20 H), 2.0 (s, 3 H), 4.05 (t, 2 H), 5.4 (m, 4 H); ^{13}C NMR δ 14.03, 20.86, 22.44, 25.51, 26.73, 27.03, 28.62, 29.29, 29.78, 32.09, 32.22, 32.52, 64.50, 129.57, 130.12, 130.24, 130.48, 170.82.

Preparation of Ketones. The following procedure for the preparation of 6-dodecanone is representative. The same reaction procedure was used as in the case of (*Z*)-5-dodecene before glacial acetic acid was added. The reaction mixture after cooling to 0 °C was directly oxidized with 30 mL of 3 N NaOH and 12 mL of 30% H_2O_2 and then refluxed for 1 h. The usual workup afforded 3.41 g (62%) of 6-dodecanone as a colorless liquid: bp 54 °C (0.2 torr) [lit.[21] bp 67–69 °C (0.7 torr)]; n^{20}_D 1.4323 (lit.[21] n^{20}_D 1.4300); IR (neat) 1715 (s), 1465 (m), 1410 (m), 1370 (m), 1125 (w), 1050 (w), 720 (w) cm^{-1}; ^1H NMR δ 0.9 (br, 6 H), 1.0–2.0 (br, 14 H), 2.35 (t, 4 H); ^{13}C NMR δ 13.98, 14.08, 22.65, 23.71, 23.98, 29.12, 31.67, 31.85, 42.83, 210.81.

6-Heneicosyn-11-one:[22] bp 140 °C (7×10^{-2} torr) [lit.[22] bp 145–150 °C (0.2 torr)]; n^{20}_D 1.4633 (lit.[22] n^{24}_D 1.4568); IR (neat) 1715 (s), 1465 (m), 1410 (m), 1370 (m), 1080 (m), 720 (w) cm^{-1}; ^1H NMR δ 0.9 (br, 6 H), 1.0–2.0 (br, 24 H), 2.0–2.7 (m, 8 H); ^{13}C NMR δ 14.15, 18.31, 18.86, 22.41, 22.88, 23.25, 24.05, 29.05, 29.53, 29.73, 31.31, 32.11, 41.32, 43.97, 79.10, 80.93, 209.71.

(*Z*)-6-Heneicosen-11-one.[23] Trimethyltin chloride (1.99 g, 10 mmol) dissolved in 10 mL of THF was used as the inducing agent to afford 1.66 g (54% yield) of (*Z*)-6-heneicosen-11-one as a colorless liquid: bp 106 °C (5×10^{-3} torr) [lit.[23] bp 175 °C (0.35 torr)]; n^{20}_D 1.4571 (lit.[23] n^{20}_D 1.4575); IR (neat) 3020 (m), 1715 (s), 1465 (s), 1420 (m), 1380 (m) cm^{-1}; ^1H NMR δ 0.9 (t, 6 H), 1.3 (br, 22 H), 1.5–2.6 (m, 10 H), 5.4 (m, 2 H); ^{13}C NMR δ 14.11, 22.73, 22.83, 23.89, 24.01, 26.74, 27.36, 29.51, 29.63, 31.70, 32.10, 42.10, 42.92, 128.81, 131.00, 210.43; mass spectrum, *m/e* 308 (parent ion). Anal. Calcd for $C_{21}H_{40}O$: C, 81.75; H, 13.07. Found: C, 81.88; H, 13.22.

(*E*)-6-Heneicosen-11-one.[24] Trimethyltin chloride (1.99 g, 10 mmol) dissolved in 10 mL of THF was used as the inducing agent to afford 1.69 g (55% yield) of (*E*)-6-heneicosen-11-one as a colorless liquid which solidified on standing: bp 130 °C (2×10^{-2} torr); mp 40–41 °C (lit.[24a] mp 36–38 °C); IR (neat) 1700 (s), 970 (s) cm^{-1}; ^1H NMR δ 0.9 (br, 6 H) 1.3 (br, 22 H), 1.5–2.2 (br, 6 H), 2.35 (t, 4 H), 5.45 (m, 2 H); ^{13}C NMR δ 14.10, 22.65, 22.76, 23.68, 23.99, 29.42, 29.58, 31.51, 32.08, 32.65, 41.98, 42.92, 129.32, 131.53, 210.82; mass spectrum, *m/e* 308 (parent ion). Anal. Calcd for $C_{21}H_{40}O$: C, 81.75; H, 13.07. Found: C, 81.59; H, 13.00.

Preparation of Alkynes. The following procedure for the preparation of 5-dodecyne is representative. The same reaction procedure was used as in the case of (*Z*)-5-dodecene before glacial acetic acid was added. Iodine (7.61 g, 30 mmol) dissolved in 20 mL of THF was then introduced via a Teflon tubing into the refluxing reaction mixture. After refluxing for 1 additional h, the usual workup afforded 2.74 g (55%) of 5-dodecyne as a colorless liquid: bp 120 °C (ca. 25 torr); n^{20}_D 1.4441; IR (neat) 1470 (m), 1390 (w), 1340 (w) cm^{-1}; ^1H NMR δ 0.9 (br, 6 H), 1.3 (br, 12 H), 2.1 (br, 4 H); ^{13}C NMR 13.67, 14.09, 18.61, 18.92, 22.09, 22.77, 28.74, 29.37, 31.59, 80.15.

1-(3-Cyclohexenyl)-3-octyne: bp 57 °C (0.1 torr); n^{20}_D 1.4819; IR (neat) 3040 (m), 1650, (w), 1430 (m), 650 (s) cm^{-1}; ^1H NMR δ 0.9 (br, 3 H), 1.5 (br, 9 H), 2.2 (br, 8 H), 5.75 (br, 2 H); ^{13}C NMR δ 13.68, 16.45, 18.58, 22.09, 25.27, 28.69, 31.49, 31.66, 32.84, 36.08, 80.04, 126.42, 127.01.

1-Phenyl-3-octyne: bp 56 °C (7×10^{-2} torr); n^{20}_D 1.5082; IR (neat) 3020 (m), 1605 (m), 1490 (m), 1450 (s) 740 (s), 690 (s) cm^{-1}; ^1H NMR δ 0.9 (br, 3 H), 1.4 (br, 4 H), 1.8–3.0 (m, 6 H), 7.3 (s, 5 H); ^{13}C NMR δ 13.63, 18.48, 21.07, 21.94, 31.26, 35.76, 79.42, 80.95, 126.13, 128.30, 128.49, 141.07.

(*E*)-10-Hexadecen-5-yne: bp 61 °C (5×10^{-3} torr); n^{20}_D 1.4587; IR (neat) 1460 (s), 1380 (m), 1330 (m), 965 (s) cm^{-1}; ^1H NMR δ 0.9 (br, 6 H), 1.3 (br, 12 H), 2.2 (br, 8 H), 5.5 (m, 2 H); ^{13}C NMR δ 13.70, 14.13, 18.34, 18.64, 22.13, 22.76, 29.38, 29.57, 31.62, 31.89, 32.81, 79.88, 80.23, 129.42, 131.32; mass spectrum, *m/e* 220 (parent ion). Anal. Calcd for $C_{16}H_{28}$: C, 87.20; H, 12.80. Found: C, 86.92; H, 12.55.

5,10-Hexadecadiyne: bp 77 °C (5×10^{-3} torr); n^{20}_D 1.4662; IR (neat) 1450 (s), 1380 (m), 1330 (m) cm^{-1}; ^1H NMR δ 0.9 (br, 6 H), 1.4 (br, 12 H), 2.3 (br, 8 H); ^{13}C NMR δ 13.68, 14.05, 18.12, 18.62, 18.89, 22.11, 22.46, 29.06, 31.32, 31.50, 79.26, 80.58; mass spectrum, *m/e* 218 (parent ion). Anal. Calcd for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found C, 87.78; H, 11.76.

8-Methyl-5-undecyne: bp 53 °C (1.5 torr); n^{20}_D 1.4407; IR (neat) 1460 (m), 1380 (m) cm^{-1}; ^1H NMR δ 0.9 (d, 9 H), 1.5 (br, 9 H) 2.2 (br, 4 H); ^{13}C NMR δ 13.68, 14.34, 18.63, 19.59, 20.44, 22.12, 26.37, 31.61, 32.89, 38.64, 78.84, 80.99.

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Registry No. **6**, 93184-58-8; **9**, 83483-57-2; 1-hexene, 592-41-6; (*Z*)-5-dodecene, 7206-28-2; (*Z*)-11-heneicosen-6-yne, 93184-59-9; (*Z*)-2-methyl-7-octadecene, 35354-39-3; (*Z*)-6-heneicosen-11-one, 54844-65-4; (*E*)-6-heneicosen-11-one, 54844-66-5; 1-(3-cyclohexenyl)-3-octyne, 93184-60-2; 1-phenyl-3-octyne, 93184-61-3; (*E*)-10-hexadecen-5-yne, 93184-62-4; 5,10-hexadecadiyne, 3508-89-2; 8-methyl-5-undecyne, 93184-63-5; (±)-disparlure, 57457-72-4; 6-heptyn-1-ol, 63478-76-2; 6-heptyn-1-ol acetate, 93184-64-6; 1-decen-4-yne, 24948-66-1; 5-methyl-1-hexene, 3524-73-0; (*Z*)-1,4-decadiene, 71612-10-7; (*E*)-1,4-decadiene, 77657-80-8; 4-vinylcyclohexene, 100-40-3; styrene, 100-42-5; 2-methyl-1-pentene, 763-29-1; 1-hexyne, 693-02-7; 1-undecyne, 2243-98-3; 6-dodecanone, 6064-27-3; 6-heneicosyn-11-one, 54844-69-8; 5-dodecyne, 19780-12-2; 1-lithio-1-hexyne, 17689-03-1; 3-heptyn-1-ol, 14916-79-1.

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