EFFICIENT STEREOSELECTIVE SYNTHESIS OF ALL GEOMETRICAL ISOMERS OF HEPTADECA-11,13-DIENES

Ales SVATOS[1] and David SAMAN[2]

Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 166 10 Prague 6, Czech Republic; e-mail: [1] svatos@uochb.cas.cz, [2] saman@uochb.cas.cz

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All geometrical isomers of heptacosa-11,13-dienes, **1–4**, previously identified in termite *Prorhinotermes simplex* cuticular hydrocarbons, were efficiently synthesized according Peterson–Hudrlik olefination procedure in high stereoisomeric purity using *syn* and *anti* elimination of *erythro* alkenyl-β-hydroxysilanes (**15** and **17**). These (*Z*)- and (*E*)-alkenyl-β-hydroxysilanes are available from regioselective opening of (1*R**,2*S**)-1,2-epoxy-1-trimethylsilylpentadecane **13** with corresponding (*Z*)- and (*E*)-dodec-1-enyl cuprates (**14** and **16**). Stereoisomeric purity of obtained dienes **1–4** was higher than 95% (^{13}C NMR).

Key words: Conjugated dienes; Stereoselective synthesis; Peterson–Hudrlik olefination; Cuticular hydrocarbons.

Recently, we investigated the composition of an epicuticular layer of *Prorhinotermes simplex* (Hagen) termites[1]. We found that hydrocarbon fractions of the extract contain large quantities of heptacosadienes. Using a combination of microchemical reactions (ozonolysis) and spectroscopic techniques (gas chromatography coupled to either mass detector or FTIR spectrometer[2]) we determined positions and geometry of double bonds in those heptacosa-11,13-dienes[1]. Now we report on the synthesis of all geometric isomers of heptacosadienes to support our determinations of geometric isomers in epicuticula of *P. simplex* termites.

Syntheses of conjugated dienes of high stereisomeric purity mostly involves C(sp^2)–C(sp^2) cross-coupling reactions of vinylic organometallics and vinylic halogenides of appropriate length usually catalyzed with transition metal complexes[3,4]. However, the synthesis of all four geometric isomers will require to prepare all the isomers of both vinylic organometallics and vinylic halogenides. This drawback can be overcome using the Alexakis procedure[5] of synthesis of conjugated dienes based on Peterson–Hudrlik olefination reaction (Scheme 1), where only one silylepoxide and both (*E*)- and (*Z*)-vinyl cuprates will be sufficient. For example, (*Z*)-hydroxy(trimethylsilyl)alkene formed by the silylepoxide opening with (*Z*)-vinyl cuprate, can by treated by either base or acid to form stereospecifically (*Z*,*Z*) and (*Z*,*E*) isomer, respectively (see Schemes 2 and 3).

EXPERIMENTAL

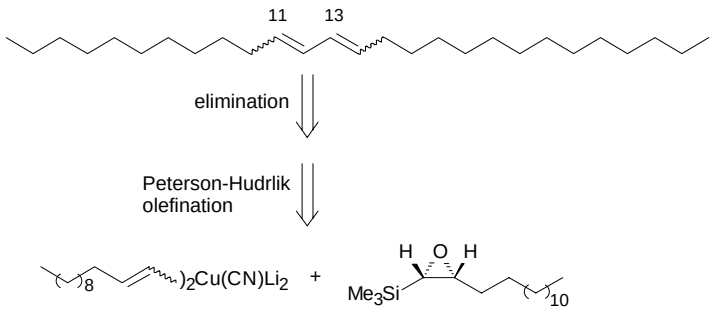
Chromatography: The synthetized substances were analyzed using a gas chromatograph HP 5890 (Hewlett–Packard) equipped with a split/splitless injector (220 °C), and with a flame ionization detector (280 °C) or a mass detector (Fisons MD 800) working in impact ionization mode, respectively. A DB-5 column (30 m × 0.25 mm, J & W Scientific) and helium gas (flow 0.7 ml/min at 50 °C) was used for the separations. The temperature program started at 60 °C (2 min delay), then the temperature of the oven was increased to 270 °C (rate 10 °C/min). Column chromatography separations were made on Merck 60 silica gel (0.040–0.063 mm) using ethyl acetate or ether in light petroleum or hexane[6].

Spectral methods: NMR spectra were determined in $CDCl_3$ solutions on Varian UNITY-500 operating at 499.9 MHz for ^1H and at 125.7 MHz for ^{13}C NMR spectra. Chemical shifts are expressed in δ (ppm) scale relative to tetramethylsilane for ^1H and relative to $CDCl_3$ signal (77.00 ppm) for ^{13}C NMR. Coupling constants are reported in Hz. Tentative assignments are denoted with an asterisk. Infrared (IR) spectra, reported in cm^{-1}, were recorded on a Bruker IFS 88 FT-IR spectrometer in CCl_4 solutions. Gas-phase infrared spectra (GC-FTIR) were taken on an HP 5890 gas chromatograph coupled to an HP 5695A IRD equipped with a narrow-band (4 000–750 cm^{-1}) infrared detector (mercury cadmium telluride). Electron impact (70 eV) mass spectra were obtained on ZAB-EQ (VG, England) instrument.

Chemicals: All chemical reactions were run in an oven dried glassware under inert atmosphere of argon or nitrogen. Tetrahydrofuran (THF), ether, and hexane were distilled from sodium benzophenone ketyl in nitrogen atmosphere. Dichloromethane was distilled from calcium hydride. Other chemicals were used as purchased. Dodec-1-yne and tridec-1-yne were obtained from Farchan Laboratories (U.S.A.). Extracts of reaction mixture were washed with aqueous sodium chloride solution, dried over $MgSO_4$ and solvents were removed on Rotavapor at 35 °C and reduced pressure (1.8 kPa).

1-Iodododec-1-yne (**6**)

A dodec-1-yne (**5**, 1.66 g, 10 mmol) solution in dry THF (10 ml) was metallated at –55 to –20 °C with butyllithium solution in hexanes (2.3 M, 3.1 ml) for 20 min. The formed solution was cooled to –45 °C, a solution of iodine (2.80 g, 11 mmol) in THF (10 ml) was added slowly, and the reaction mixture was allowed to warm up to 20 °C. The obtained white suspension was treated with saturated aqueous ammonium chloride solution (5 ml), the mixture extracted with pentane (2 × 20 ml), combined extracts were successively washed with Na_2SO_3 and NaCl aqueous saturated solutions (10 ml each), and organic phase was dried. The pentane solution was passed thorough short silica gel column



SCHEME 1

(10 g), and pentane was then evaporated. The obtained iodide **6** (2.52 g, 86 %) was used in the hydroboration step without any purifications.

(*Z*)-1-Iodododec-1-ene (**7**)

Dicyclohexylborane was prepared[7,8] in THF (10 ml) from borane dimethylsulfide complex (*ca* 10 M, 1.4 ml) and cyclohexene (2.36 g, 28 mmol). The obtained white suspension was treated at 0 °C with a solution of **6** (2.50 g, 8.56 mmol) in THF (10 ml). The obtained mixture was stirred at 0 °C for 30 min and at 20 °C for additional 30 min. The formed vinylborane was hydrolyzed with acetic acid (4 ml) at 20 °C for 20 h, the reaction mixture was neutralized with sodium hydroxide (3 M, 20 ml), and carefully treated with aqueous hydrogen peroxide (30%, 4 ml). Product was extracted with pentane (2 × 20 ml). Column chromatography on silica gel (300 g) in pentane yielded iodide **7** (1.91 g, 65% on **5**) in 97% isomeric purity (GC). ^{1}H NMR spectrum: 0.88 t, 3 H, J = 7.3 (3 × H-12); 1.20–1.40 m 16 H (2 × H4 to H11); 2.08 dt, 2 H, J = 7.3, 7.0 (2 × H-3); 6.17 m, 2 H (H-1, H-2). Mass spectrum, *m/z* (%): 294 (M^+, 17), 167 (M^+ – 127, 14), 111 (18), 97 (43), 83 (56), 69 (56), 57 (47), 55 (78), 43 (84), 41 (100), 39 (37), 29 (46). IR spectrum (CCl_4): 3 073 (=C–H); 1610 (C=C); 1 378 (CH_3); 690 (=C–H); 628 (C–I). For $C_{12}H_{23}I$ (294.2) calculated: 48.99% C, 7.88% H, 43.13% I; found: 49.30% C, 8.11% H 42.91% I.

(*E*)-1-Iodododec-1-ene (**8**)

A solution of **5** (1.66 g, 10 mmol) in dry hexane (10 ml) was treated with diisobutylaluminium hydride (Dibal-H, 1 M solution in toluene, 12 ml) at 55 °C for 5 h, cooled to –55 °C and a solution of iodine (2.79 g, 11 mmol) in dry THF (10 ml) was added during 6 min. After warming to room temperature, the reaction mixture was poured into a separation funnel containing ice-cold mixture of saturated aqueous solutions of ammonium chloride and sodium thiosulfate (3 : 1, 20 ml). The formed salts were removed on Celite pad (5 g), which was washed with pentane (3 × 15 ml). The combined pentane extracts were washed with 10% sulfuric acid (15 ml), water (2 × 15 ml) and saturated aqueous sodium chloride solution (15 ml). Solvents were evaporated and the residue distilled, iodide **8**, b.p. 90 °C/160 Pa, yield 2.3 g (78%) was obtained in 99.7% isomeric purity (GC). ^{1}H NMR spectrum: 0.88 t, 3 H, J = 6.7 (3 × H-12); 1.20–1.40 m, 16 H (2 × H4 to H11); 2.04 dt, 2 H, J = 7.3, 7.0 (2 × H-3); 5.97 dt, 1 H, J = 14.3, 1.5 (H-1); 6.51 dt, 1 H, J = 14.3, 7.3 (H-2). Mass spectrum, *m/z* (%): 294 (M^+, 23), 167 (M^+ – 127, 26), 111 (16), 97 (38), 83 (56), 69 (55), 57 (52), 55 (68), 43 (91), 41 (100), 39 (42), 29 (54). IR spectrum (CCl_4): 3 051 (=C–H); 1 606 (C=C); 1 378 (CH_3); 946 (=C–H); 661 (C–I). For $C_{12}H_{23}I$ (294.2) calculated: 48.99% C, 7.88% H, 43.13% I; found: 49.01% C, 8.11% H, 43.14% I.

1-(Trimethysilyl)pentadec-1-yne (**10**)

A pentadec-1-yne (**9**, 2.08 g, 10 mmol) solution in dry THF (15 ml) was metallated at –55 to –20 °C with butyllithium solution in hexanes (2.3 M, 3.1 ml) for 20 min and the reaction mixture was stirred for additional 20 min at room temperature. The obtained white suspension was cooled to –10 °C and the suspension was treated with a chlorotrimethylsilane (1.88 ml, 15 mmol) solution in THF (2.5 ml) and the reaction mixture was stirred for 30 min at –10 to 20 °C. The reaction mixture was treated with ammonium chloride aqueous solution (10 ml), and extracted with pentane (3 × 15 ml). Silane **10** (2.65 g, 95% yield) was obtained in 96% purity (GC). ^{1}H NMR spectrum: 0.15 s, 9 H ($(CH_3)_3Si$); 0.88 t, 3 H, J = 6.7, (3 × H-15); 1.20–1.40 m, 20 H (2 × H-5 to H-14); 1.51 m, 2 H (2 × H-4); 2.21 t, 2 H, J = 7.0 (2 × H-3). Mass spectrum, *m/z* (%): 280 (M^+, 7), 265 (M^+ – 15, 30), 206 (11), 182 (7), 168 (17), 154 (25), 73 (100), 59 (28), 43 (21). IR spectrum (CCl_4): 2 174 (C≡C); 1 378 (CH_3); 1 250,

843, 854, 639 (Si–CH_3). For $C_{18}H_{36}Si$ (280.6) calculated: 77.06% C, 12.93% H; found: 77.16% C, 13.03% H.

(*Z*)-1-(Trimethysilyl)pentadec-1-ene (**11**)

A solution of **10** (1.00 g, 3.57 mmol) in dry ether (11 ml) was treated with Dibal-H solution in hexanes (1 M, 4 ml) at 0 °C during 6 min. The obtained solution was stirred 5.5 h at room temperature, cooled to 0 °C and carefully quenched with ammonium chloride aqueous solution (4 ml). The formed white precipitate was filtered thorough Celite pad (1 g), which was thoroughly washed with dry ether (3 × 20 ml). The combined ether washes were evaporated. The reaction mixture was analyzed by GC, conversion was 84%. The crude product was purified on a silica gel (200 g) column, eluted with pentane and pentane–ether (98.5 : 1.5) mixture, it furnished **11** (0.77 g, 77%) in 99.7% stereoisomeric purity (GC). ^{1}H NMR spectrum: 0.11 s, 9 H (($CH_3)_3$Si); 0.88 t, 3 H, *J* = 6.8, (3 × H-15); 1.20–1.40 m, 20 H (2 × H-5 to H-14); 1.55 m, 2 H (2 × H-4); 2.10 dt, 2 H, *J* = 7.3, 6.8 (2 × H-3); 5.46 dt 1 H, *J* = 14.0, 1.2 (H-1); 6.30 dt 1 H, *J* = 14.0, 7.3 (H-2). Mass spectrum, *m/z* (%): 282 (M^+, 6), 267 (M^+ – 15, 44), 210 (5), 208 (5), 125 (8), 114 (48), 99 (20), 97 (18), 83 (22), 73 (100), 59 (43), 43 (36). IR spectrum (CCl_4): 1 606 (C=C); 1 378 (CH_3); 1 248, 838, 858 (Si–CH_3). For $C_{18}H_{38}Si$ (282.6) calculated: 76.51% C, 13.55% H; found: 76.69% C, 12.90% H.

Dibal-H Reductions of Acetylene **10** in Hexane

a) *At 20 °C*. A solution of **10** (1.00 g, 3.57 mmol) in dry hexane (4 ml) was treated at 0 °C with Dibal-H solution in hexane (1 M, 4 ml). The obtained mixture was stirred for 4 h at 20 °C and quenched as it was described above. Gas chromatography and ^{1}H NMR spectroscopy indicated 50/50 proportion of (*E*)-1-(trimethylsilyl)pentadec-1-ene (**12**) and its isomer **11**. ^{1}H NMR data for **12** (isolated by silica gel column chromatography): 0.04 s, 9 H (3 × CH_3); 0.88 t, 3 H, *J* = 7.0 (3 × H-15); 1.20–1.40 m, 20 H (2 × H5 to H14); 1.55 m, 2 H (2 × H-4); 2.10 m, 2 H (2 × H-3); 5.61 dt, 1 H, *J* = 18.6, 1.4 (H-1); 6.03 dt 1 H, *J* = 18.6, 6.1 (H-2). IR spectrum (CCl_4): 1 615 (C=C); 1 378 (CH_3); 1 248, 839, 858 (Si–CH_3).

b) *At 60 °C*. The experiment was performed as in *a*), but the mixture was heated at 60 °C for 3 h. Gas chromatography and ^{1}H NMR spectroscopy indicated 70/30 proportion of isomers **12** and **11**.

(1*R**,2*S**)-1,2-Epoxy-1-trimethylsilylpentadecane (**13**)

A suspension of 3-chloroperbenzoic acid (MCPBA, 85%, 0.61 g, 3 mmol) and sodium hydrogenphosphate (1.14 g, 3 mmol) in dry dichloromethane (35 ml) was treated with a solution of vinylsilane **11** in CH_2Cl_2 (5 ml, ref.[5]). The mixture was stirred at room temperature for 5 h then poured over Celite pad (2 g) and the pad was washed with dichloromethane (3 × 5 ml). The combined extracts were washed with sodium sulfite aqueous solution (3 × 10 ml) and dried. The chromatographic purification (50 g of silica gel, hexane–ether 8 : 2) provided **13** (0.608 g, 77% yield, 99% *cis*, GC) and unreacted **11** (0.140 g, 19%). ^{1}H NMR spectrum: 0.13 s, 9 H (($CH_3)_3$Si); 0.88 t, 3 H, *J* = 7.0 (3 × H-15); 1.20–1.40 m, 16 H (2 × H-4 to H-11); 1.48 m, 2 H (2 × H-3); 2.19 d, 1 H, *J* = 5.2 (H-1); 3.04 m, 1 H, (H-2). Mass spectrum, *m/z* (%): 298 (M^+, 0.5), 283 (M^+ – 15, 7), 185 (8), 143 (14), 129 (100), 115 (10), 95 (8), 82 (13), 75 (47), 73 (94), 59 (12), 55 (10), 43 (24), 41 (20). IR spectrum (CCl_4): 1 378 (CH_3); 1 250, 843, 854, 639 (Si–CH_3); 1 263, 881 (epoxide ring). For $C_{18}H_{38}OSi$ (298.6) calculated: 72.41% C, 12.83% H; found: 72.28% C, 12.60% H.

(11*Z*,13*R**,14*R**)-14-Hydroxy-13-(trimethylsilyl)heptacos-11-ene (**15**)

a) *Preparation of (Z)-dodec-1-enyl(dilithiumcyano)cuprate(I)* (**14**). A solution of iodide **7** (210 mg, 0.71 mmol) in dry ether (1.5 ml) was treated at –70 °C with butyllithium solution in hexanes (2.5 M, 0.270 ml) during 5 min. The mixture was stirred at –70 to –40 °C for 25 min. Then the flow of argon was increased, the septum was removed, copper(I) cyanide (33.5 mg, 0.375 mmol) was rapidly, in one portion, added to the obtained clear solution, and the septum returned on the reaction vial. The suspension was stirred for 40 min at –40 to –32 °C forming greenish solution of cuprate **14**.

b) *Opening of epoxide* **13.** The above prepared solution of **14** was recooled to –70 °C and a solution of epoxide 13 (71 mg, 0.24 mmol) in dry ether (1 ml) followed after 5 min with a solution of boron trifluoride etherate (37 μl, 0.26 mmol) in dry ether (0.5 ml) was added. The mixture was stirred at –70 to –55 °C for 1.5 h and then quenched with saturated aqueous solution of ammonium chloride (1 ml). After stirring for 30 min and removing a cooling bath the mixture was extracted with ether (3 × 5 ml), the combined organic extracts were washed with a mixture of ammonium chloride and ammonium hydroxide concentrated aqueous solutions (2 : 1, 3 × 3 ml) and dried. Crude product obtained after evaporation of solvents was purified by a column chromatography on Florisil (10 g) eluted with light petroleum, and light petroleum–ether mixtures (95 : 5 and 80 : 20) affording **15** (61 mg, 55% yield on **13**). ^{13}C NMR spectrum: –1.8 ($(CH_3)_3Si$), 14.08 (C-1, C-27), 22.66 (C-2, C-26), 26.01 (C-10*), 27.72 (C-16*), 29.34, 29.49, 29.53, 29.58, 29.63, 29.67, 29.82 (C-4 to C-9, C-17 to C-24), 31.91 (C-3, C-25), 35.67 (C-13), 37.37 (C-15), 72.1 (C-14), 125.9 (C-12), 131.1 (C-11). ^{1}H NMR spectrum: 0.04 s, 9 H ($(CH_3)_3Si$); 0.88 t, 6 H, *J* = 7.1 (3 × H-1, 3 × H-27); 1.20–1.28 m, 38 H (2 × H-2 to 2 × H-9, 2 × H-16 to 2 × H-26); 1.91 m, 2 H (2 × H-10); 1.94 dd, 1 H, *J* = 5.4, 11.7 (H-13); 2.02 m, 2 H (2 × H-15); 3.75 m, 1 H (H-14); 5.35 ddt, 1 H *J* = 11.5, 11.5, 1.5 (H-12); 5.46 ddd, 1 H, *J* = 6.3, 7.8, 11.0 (H-11).

(11*Z*,13*Z*)-Heptacosa-11,13-diene (**1**)

A solution of hydroxysilane **15** (26 mg, 0.056 mmol) in THF (0.5 ml) was added at room temperature in vigorously stirred suspension of sodium hydride (50% in mineral oil, 16 mg, 0.33 mmol) in dry THF (0.5 ml) and stirred for 1 h. Then saturated aqueous ammonium chloride solution (0.5 ml) was added, stirred for 20 min and extracted with ether (2 × 3 ml). Purification of crude diene (18.3 mg) on Florisil (2 g) column eluted with hexane afforded pure **1** (12.4 mg, 59% yield). NMR, IR and MS data are reported in Tables I, II and III, respectively. High resolution MS: for $C_{27}H_{52}$ calculated: 376.406902; found: 376.410800.

(11Z,13*E*)-Heptacosa-11,13-diene (**2**)

A solution of hydroxysilane **15** (28 mg, 60 mmol) in dry dichloromethane (0.5 ml) was treated at –20 °C with boron trifluoride etherate (15 μl, 120 μmol) solution in dry dichloromethane (1 ml) for 1 h. The reaction was stopped by adding a mixture of ammonium chloride–ammonium hydroxide saturated aqueous solutions (2 : 1, 0.5 ml), extracted with ether (3 × 5 ml) and subsequent chromatography on Florisil (2 g) eluted with hexane provided **2** (21.5 mg, 95% yield). NMR, IR and MS data are reported in Tables I, II and III, respectively. High resolution MS: for $C_{27}H_{52}$ calculated: 376.406902; found: 376.413400.

(11*E*,13*R**,14*R**)-14-Hydroxy-13-(trimethylsilyl)heptacos-11-ene (**17**)

(*E*)-Dodec-1-enyl(dilithiumcyano)cuprate(I) (**16**) was prepared from iodide **8** (262 mg, 0.89 mmol), butyllithium solution in hexanes (2.5 M, 0.356 ml) and copper(I) cyanide (42 mg, 0.467 mmol) as was described above for **14**. The formed cuprate **16** was added at –70 °C to a solution epoxide **13**

(88 mg, 0.30 mmol) in dry ether (1.5 ml) followed with addition of boron trifluoride etherate (41 μl, 0.33 mmol). The β-hydroxysilane **17** (81.4 mg, 58% yield on **13**) was purified using Florisil (4 g) column. ^{13}C NMR spectrum: –1.8 ($(CH_3)_3Si$), 14.08 (C-1, C-27), 22.66 (C-2, C-26), 25.74 (C-10*), 25.81 (C-16*), 29.34, 29.49, 29.54, 29.58, 29.64, 29.67, 29.87 (C-4 to C-9, C-17 to C-24), 31.91 (C-3, C-25), 35.24 (C-13), 37.15 (C-15), 71.73 (C-14), 126.8 (C-12), 132.3 (C-11). ^{1}H NMR spectrum: 0.03 s, 9 H ($(CH_3)_3Si$); 0.88 t, 6 H, J = 7.0 (3 × H-1, 3 × H-27); 1.20–1.4 m, 38 H (2 × H-2 to 2 × H-9, 2 × H-16 to 2 × H-26); 1.4–1.6 m, 3 H (H-13, 2 × H-15); 2.03 m, 2 H (2 × H-10); 3.72 m, 1 H, (H-14); 5.32 m, 2 H (H-11, H-12).

(11*E*,13*Z*)-Heptacosa-11,13-diene (**3**)

Diene **3** was obtained from hydroxysilane **17** (23 mg, 49 μmol) and NaH suspension (Fluka, 50% in mineral oil, 6.5 mg, 120 μmol) following the procedure for preparation of diene **1**, yield 10.8 mg, 59%. NMR, IR and MS data are reported in Tables I, II and III, respectively. High resolution MS: for $C_{27}H_{52}$ calculated: 376.406902; found: 376.409400.

(11*E*,13*E*)-Heptacosa-11,13-diene (**4**)

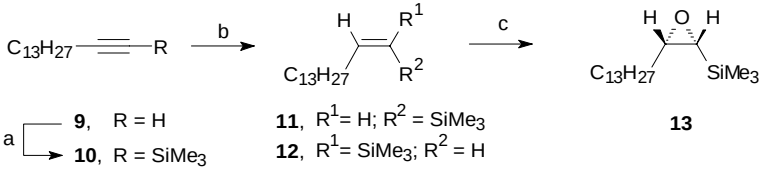
Diene **4** was obtained from hydroxysilane **17** (26.4 mg, 57 μmol) dissolved in dichlormethane (0.5 ml) and treated at –20 °C with boron trifluoride etherate (15 μl, 120 μmol) solution in dichloromethane (1 ml) following the procedure for preparation of **2**, 14.9 mg (69%) was obtained. NMR, IR and MS data are reported in Tables I, II and III, respectively. High resolution MS: for $C_{27}H_{52}$ calculated: 376.406902; found: 376.401600.

TABLE I
^{13}C NMR data for conjugated dienes **1–4**

Carbon	Chemical shifts (δ) in ppm (ref. 77.00 ppm)			
	(*Z*,*Z*)-**1**	(*Z*,*E*)-**2**	(*E*,*Z*)-**3**	(*E*,*E*)-**4**
1, 27	14.07	14.08	14.08	14.08
2, 26	2 × 22.66	2 × 22.66	2 × 22.66	2 × 22.66
3, 25	31.89, 31.91	2 × 31.91	2 × 31.91	2 × 31.91
10	27.48	27.68	32.86	32.59
11	132.10	130.11	134.70	132.43
12	123.61	128.62	125.65	130.38
13	123.61	125.64	128.63	130.38
14	132.10	134.70	130.12	132.43
15	27.48	32.86	27.68	32.59
4–9, 16–24	29.28, 29.31, 2 × 29.34, 3 × 29.50, 4 × 29.60, 4 × 29.65	29.23, 29.26, 29.36, 29.41, 2 × 29.51, 2 × 29.61, 2 × 29.64, 4 × 29.66, 29.73	29.23, 29.26, 29.32, 3 × 29.41, 2 × 29.51, 29.61, 2 × 29.64, 3 × 29.66, 29.73	2 × 29.22, 29.31, 29.36, 2 × 29.44, 2 × 29.51, 3 × 29.59, 4 × 29.65

RESULTS AND DISCUSSION

The synthesis of isomers **1–4** are given in Schemes 2 and 3. The (*Z*)-1-iodododec-1-ene (**7**) was prepared using hydroboration of iodoacetylene **6** with dicyclohexylborane[8] prepared from borane–dimethylsulfide complex and cyclohexene. The stereoisomeric purity of **7** was 97% of *Z*-isomer. The (*E*)-1-iodododec-1-ene (**8**) was prepared in high stereoisomeric purity (99.7%) using hydroalumination[9] with diisobutylaluminium



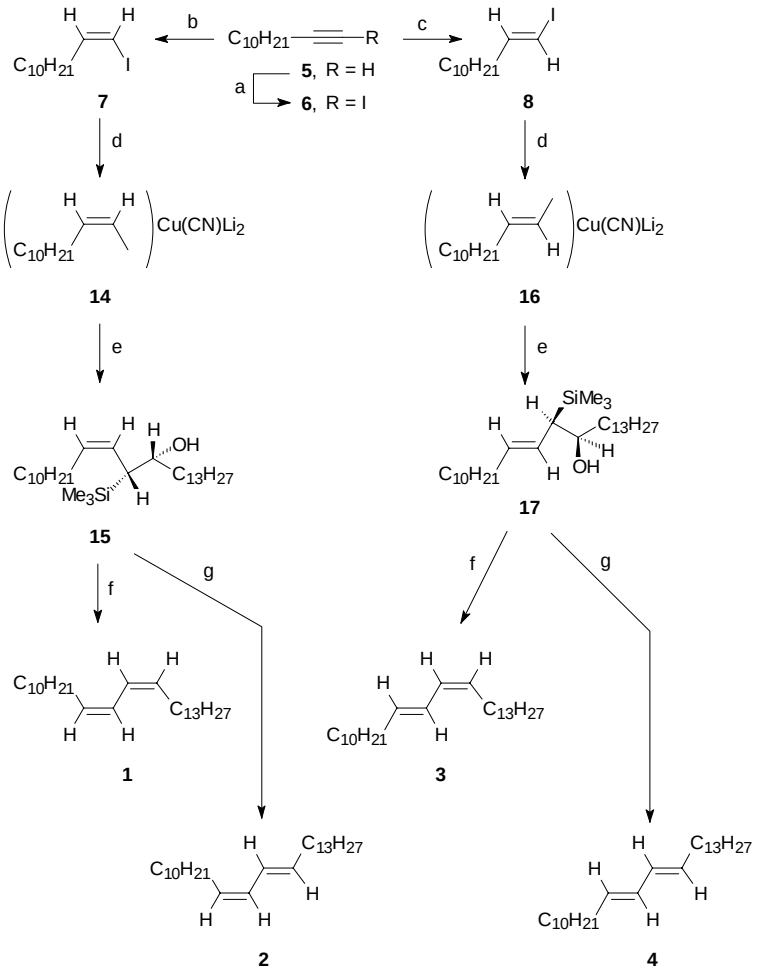
a) BuLi/Me_3SiCl/THF; b) iBu_2AlH/ether/$H^{\oplus}$;
c) MCPBA/Na_2HPO_4/CH_2Cl_2

SCHEME 2

TABLE II
^{1}H NMR data for conjugated dienes **1–4**

Proton	Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz			
	(*Z*,*Z*)-**1**	(*Z*,*E*)-**2**	(*E*,*Z*)-**3**	(*E*,*E*)-**4**
1, 27	0.88 t *J* = 7.0	0.88 t *J* = 7.0	0.88 t *J* = 7.1	0.88 t *J* = 7.1
2, 26	1.37 m	1.36 m	1.37 m	1.36 m
10	2.16 dt *J* = 7.3, 7.3	2.09 ddt *J* = 1.0, 7.5, 7.3	2.15 ddt *J* = 1.7, 7.3, 7.3	2.04 dt *J* = 6.8, 7.1, 7.3
11	5.44 m	5.30 dt *J* = 7.5, 10.7	5.65 dt *J* = 6.9, 7.1, 15.1	5.56 m
12	6.24 m	5.94 ddt *J* = 11.0, 11.0, 1.2	6.29 dddt *J* = 1.2, 1.5, 10.9, 14.6	5.99 m
13	6.24 m	6.29 dddt *J* = 1.2, 1.2, 11.0, 15.1	5.94 ddt *J* = 11.0, 11.0, 1.2	5.99 m
14	5.44 m	5.65 dt *J* = 7.1, 7.1, 15.1	5.30 dt *J* = 7.5, 10.7	5.56 m
15	2.16 dt *J* = 7.3, 7.3	2.15 ddt *J* = 1.7, 7.3, 7.3	2.09 ddt *J* = 1.0, 7.5, 7.3	2.04 dt *J* = 6.8, 7.1, 7.3
3–9 16–25	1.2–1.4 m	1.2–1.4 m	1.2–1.4 m	1.2–1.4 m

(Dibal-H) in hexane followed by iodination of the formed vinylic diisobutylaluminium. Hydroalumination step was also used for the preparation of **11**. We found that high stereoisomeric purity, 99.7% (*Z*), can only be achieved using ether[10] as a co-solvent. When hexane was used as a solvent a mixture of *Z* and *E* isomers (**11** and **12**) was obtained. The formation of *E* isomer **12** was more favored at elevated temperature (70% at 60 °C compared to 50% at 20 °C). We suppose, in accordance with the lite-



a) BuLi/I_2/THF; b) $(C_6H_{12})_2$BH/AcOH/THF; c) iBu_2AlH/I_2/hexane; d) 1. BuLi/hexane/ether, 2. CuCN/ether/-78 °C; e) **13**, $BF_3.Et_2O$/-70 °C to -55 °C/NH_4Cl aqueous solution; f) NaH/THF/20 °C; g) $BF_3.Et_2O/CH_2Cl_2$/-20 °C

SCHEME 3

TABLE III
Infrared and mass-spectral data for dienes **1–4**

Vibration	Spectral data			
	(*Z*,*Z*)-**1**	(*Z*,*E*)-**2**	(*E*,*Z*)-**3**	(*E*,*E*)-**4**
	FT-IR spectra in liquid phase[a]			
=C–H str	3 037 (87.5) 3 005 (83.0)	3 020 (89.5)	3 019 (90.8)	3 014 (86.0)
CH_3, CH_2 asym str	2 956 (38.0) 2 927 (5.0)	2 957 (61) 2 927 (17.5)	2 957 (62) 2 927 (19.0)	2 957 (47.6) 2 927 (8.8)
CH_3, CH_2 sym str	2 872 (16.0)	2 872 (37.5)	2 872 (38.0)	2 872 (24.2)
CH_2 def	1 467 (62.5)	1 467 (78.0)	1 467 (78.0)	1 467 (70.8)
CH_3 def	1 378 (89.2)	1 378 (92.0)	1 378 (93.5)	1 378 (90.0)
=C–H wag		983 (89.0)	984 (89.8)	988 (60.0)
=C–H wag		948 (89.2)	948 (91.6)	
	FT-IR spectra in gas phase[b]			
=C–H str	3 032 (99.51) 3 005 (99.29) sh	3 014 (99.45)	3 014 (99.71)	3 013 (99.74)
CH_3, CH_2 asym str	2 932 (99.29)	2 933 (92.62)	2 933 (99.12)	2 933 (96.19)
CH_3, CH_2 sym str	2 864 (96.16)	2 864 (97.21)	2 864 (99.12)	2 864 (98.62)
CH_2 def	1 460 (99.30)	1 461 (99.51)	1 460 (99.80)	1 459 (99.77)
CH_3 def	1 352 (99.75)	1 351 (99.81)	1 348 (99.89)	1 350 (99.92)
=C–H wag		978 (99.75)	978 (99.88)	982 (99.73)
=C–H wag		948 (99.80)	948 (99.89)	
	MS (EI, 70 eV) *m/z* (rel. int.)			
	376 (M^+,67), 236 (10), 222 (7), 208 (17), 194 (15), 180 (12), 166 (28), 152 (15), 137 (16), 123 (26), 109 (39), 97 (47), 96(100), 95 (63), 83 (53), 82 (94), 81 (76), 69 (46), 67 (97), 57 (46), 55 (59), 43 (77), 41 (49)	376 (M^+,100), 236 (7), 222 (4), 208 (12), 194 (11),180 (7), 166 (31), 152 (10), 137 (12), 123 (22), 109 (35), 97 (36), 96(83), 95 (56), 83 (45), 82 (82), 81 (63), 69 (35), 67 (86), 57 (34), 55 (42), 43 (55), 41 (32)	376 (M^+,65), 236 (8), 222 (7), 208 (17), 194 (13),180 (10), 166 (23), 152 (14), 137 (16), 123 (26), 109 (41), 97 (46), 96(100), 95 (66), 83 (58), 82 (96), 81 (76), 69 (49), 67 (94), 57 (54), 55 (65), 43 (77), 41 (57)	376 (M^+,76), 236 (7), 222 (6), 208 (17), 194 (13), 180 (10), 166 (27), 152 (12), 137 (15), 123 (26), 109 (41), 97 (54), 96 (97), 95 (66), 83 (63), 82 (96), 81 (74), 69 (53), 67 (100), 57 (51), 55 (58), 43 (66), 41 (47)

[a] Peak positions in cm^{-1} (percent transmission); [b] resolution 8 cm^{-1}, peak positions in cm^{-1} (percent transmission).

rature[11], that diisobutyl(dodec-11-yl)aluminium, formed by *syn* attack of Dibal-H on triple bond of **10**, is thermally isomerized to isolated *Z/E* mixtures. In the presence of Lewis bases (*e.g.* ether in our case) the isomerisation is effectively suppressed and (after aqueous work-up) only product of the initial *syn* addition can be isolated. Isomerically pure **11** was converted to epoxide **13** using the Alexakis procedure[5]. The final stereoisomeric purity of **13** after chromatography on silica gel was 99%.

Cyanocuprates **14** and **16** were prepared from iodides **7** and **8**, *via* halogen–metal exchange using butyllithium. They were used to open epoxide **13** in the presence of boron trifluoride etherate. The formed pentadecenyl-β-hydroxysilanes **15** and **17** were separated from nonpolar monoenic and dienic by-products (arising from acidic degradation of cuprates and hydroxysilanes) on Florisil columns. This purification step ensured a high stereoisomeric purity of conjugated dienes. Finally, dienes **1–4** were formed by either basic (NaH) *syn*-elimination[5] or acidic (BF_3 . Et_2O) *anti*-elimination[5]. Purity of prepared dienes was determined to be more than 95% using ^{13}C NMR spectroscopy. The stereoisomeric purity of prepared dienes can not be reliably determined using GC chromatography due to pronounced isomerization of dienes in a GC injector.

We were curious whether we can see any differences in ^{13}C NMR spectra of *Z,E* isomer **2** and *E,Z* isomer **3**. Those isomers can not be distinguished[2] using gas phase FT IR in the cases where double bonds are in/or near of the center of the chain. However, as we can see in the Table I dienes **2** and **3** have identical ^{13}C NMR spectra. Also ^{1}H NMR spectral characteristic are identical (Table II). In the cases where a molecule is less symmetric, *e.g.* dodeca-6,8-dien-1-ols isomers, the carbon NMR spectra of isomers are still fully distinguishable for particular isomer[12]. Additionally, the effect of "almost" symmetric molecule (carbon chains in hexadeca-11,13-dienes differ in three carbon atoms) can be seen in ^{13}C NMR spectra of dienes **1** and **4** where only two peaks for four dienic carbons were detected. Neither MS nor IR spectra (both gas-phase and in solution) for **2** and **3** displayed significant differences.

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