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HIGHLY STEREO- AND REGIOSELECTIVE PALLADIUM-CATALYZED SYNTHESES OF (3E,5Z)-, (3E,5E)-, AND (3Z,5E)-1,3,5-UNDECATRIENE

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Abstract: (3E,5Z)-1,3,5-Undecatriene (3) having 98.2% stereoisomeric purity has been prepared by a new and expeditious route involving two selective Pd-catalyzed carbon-carbon bond forming reactions. The key step of this synthesis is a highly diastereoselective Pd-catalyzed cross-coupling reaction between 1-heptynylzinc chloride (11a) and a molar excess of (E)/(Z)-1,2-dibromoethylene (12). Another highly diastereoselective Pd-catalyzed reaction, which involves a cross-coupling between trimethylsilylethynylzinc chloride (15) and molar excesses of stereoisomeric mixtures of 1-bromo-1-alkenes (16), has been used to prepare (E)-1-trimethylsilyl-3-nonen-1-yne (10a), a key intermediate for the synthesis of (3E,5E)- and (3Z,5E)-1,3,5-undecatriene, (4) and (5). Compounds 3 and 4, isolated from the essential oil of Ferula galbaniflua, also occur together with compound 5 in the male attracting oils of seaweeds. These substances have odors highly appreciated in perfumery.

Stereodefined conjugated straight-chain polyenes containing terminal vinyl units are widely distributed in Nature and show interesting biological properties. For example, (Z)- and (E)-9,11-dodecadien-1-yl acetate, 1 and 2, are sex pheromone components of Diparopsis castanea[1]; (3E,5Z)- and (3E,5E)-1,3,5-undecatriene, 3 and 4, isolated from the essential oil of Ferula galbaniflua[2], also occur, together with (3Z,5E)-1,3,5-undecatriene (5) and (3E,5E,8Z)- and (3E,5Z,8Z)-1,3,5,8-undecatetraene, 6 and 7, in the male attracting essential oil of the seaweeds Dictyopteris plagiogramma, D. australis[3] and D. membranacea[4]. Moreover, compound 6 has been isolated as a gamete secretion in Spermatochnus paradoxus[5] and (3E,5Z)-1,3,5-octatriene (8) has been characterized as the male attractant of the oögamus seaweed Fucus serratus[6]. It is also interesting to note that trienes 3 and 4 exhibit odors which are highly appreciated in perfumery[7] and that triene 3 is a flavor compound present in celery, parsley, mandarin, apple and pear[8].

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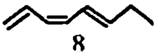

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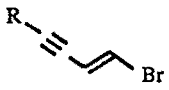
The study of the biological activity of these rather unstable substances, which are accessible in only very small amounts from natural sources, requires efficient and flexible syntheses of these polyenes and related compounds. However, whereas considerable attention has been devoted in the past few years to develop stereospecific syntheses of terminal conjugated (Z)- and (E)-dienes, and particularly of compounds 1 and 2[9-12], few studies have been carried out on the stereocontrolled synthesis of stereodefined terminal 1,3,5-trienes. These studies regard a stereoselective preparation of compounds 3 and 4 by thermal extrusion of SO_2 from stereodefined alkenylsulfolenes generated in situ by a retro Diels-Alder reaction[13], anather synthesis of 4 starting from an (E)-2,4-pentadienylcarbamate[10], and a preparation of (3Z,5E)-1,3,5-undecatriene (5) of unknown stereoisomeric purity by a thermal isomerization of (Z)-1,2,4-undecatriene[14]. Moreover, very recently, while this manuscript was in preparation, simple and efficient stereoselective syntheses of compounds 3 and 4, which utilize an (E)-1-chloro-3-alkyn-1-ene and a (3E,5E)-1-chloro-1,3-alkadiene, respectively, as key intermediates, have been reported[15].

As part of our studies on the stereospecific or stereoselective synthesis of stereodefined biologically active compounds[16], we now report simple and expeditious regio- and stereocontrolled syntheses of compounds 3, 4 and 5, which involve applications of two highly diastereoselective palladium-catalyzed carbon-carbon bond forming reactions developed recently in our laboratory[17,18]. These reactions give rise to (E)-1-bromo-3-alkyn-1-enes (9) and (E)-1-trimethylsilyl-3-alken-1-ynes (10), respectively.



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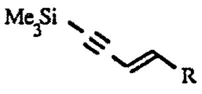

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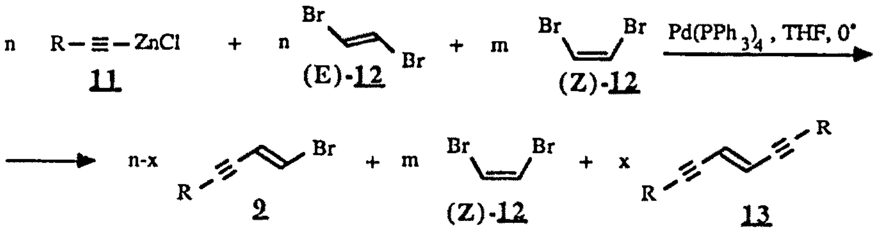
Results and Discussion

The method developed to prepare (3E,5Z)-1,3,5-undecatriene (3) was based on a convergent strategy involving a Pd-catalyzed coupling reaction between an (E)-1-bromo-3-yn-1-ene (9) and vinylzinc chloride, followed by the (Z)-stereoselctive reduction of the (E)-1,3-dien-5-yne so obtained.

The preparation of the required alkynenyl bromide of (E)-configuration was performed by an improvement of the general method reported in Scheme 1.

SCHEME 1

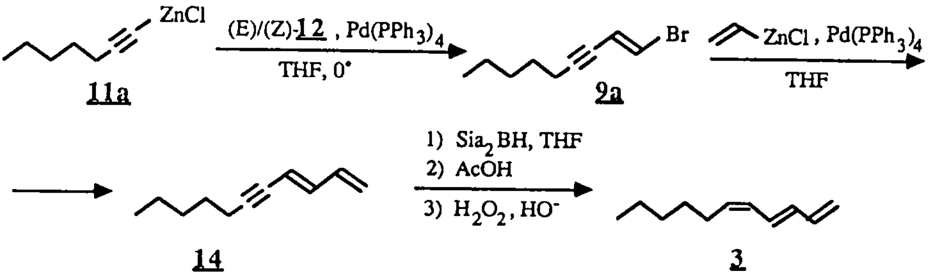


In fact, we had previously reported briefly[17] that, when treated with n equiv of an 1-alkynylzinc chloride (11) and 2 mole% of $Pd(PPh_3)_4$ in THF at 0° for 16 h, a diastereoisomeric mixture of commercially available 1,2-dibromoethylene (12) which contains n equiv of (E)-12, affords in modest yields (E)-1-bromo-3-yn-1-enes (9) having high stereoisomeric purity, together with significative amounts of the corresponding (E)-1,5-diyn-3-enes (13).

A significative improvement of the selectivity of this diastereoselective monoalkynylation reaction was obtained by treatment of n equiv of 11 with a THF solution of (E)/(Z)+12 which contained 2n equiv of (E)-12. In fact, using this procedure it was possible to prepare (E)-1-bromo-3-nonyn-1-ene (9a) in 58% isolated yield . Gas-chromatography coupled with mass-spectrometry indicated that 9a, after isolation, had stereoisomeric purity higher than 97%. The undesired dialkynylation reaction product, which was stereoisomerically pure, was obtained in 17% yield.

Then, compound 9a was converted into triene 3 according to the reaction sequence reported in Scheme 2.

SCHEME 2

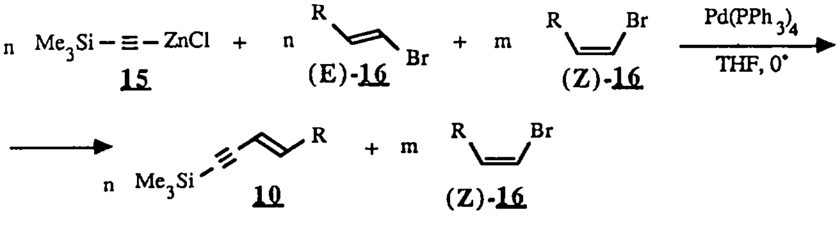


The cross-coupling reaction of 9a with vinylzinc chloride, in the presence of a catalytic amount of Pd(PPh$_3$)$_4$, gave rise in 73% yield to (E)-1,3-undecadien-5-yne (14) which had 96% stereoisomeric purity. Treatment of 14 with disiamylborane, followed by protonolysis and reaction with hydrogen peroxide and 6 N NaOH, gave, after purification by liquid chromatography followed by fractional distillation, compound 3 in 75% yield. Glc analysis showed that 3 had 98.2% stereoisomeric purity. Such compound, which was characterized by ^{1}H NMR, IR, and mass spectrometry, exhibited spectral properties in good agreement with those reported for 3 in the literature[14].

Taking into account these results, the above synthesis of 3 resulted superior to that based on the SO$_2$extrusion from a (Z)-alkenylsulfolene[13], and to the method reported recently by Ratovelomanana and Linstrumelle[15], which afford the desired triene with 91 and 95% stereoisomeric purity, respectively.

The strategies devised to prepare (3E,5E)- and (3Z,5E)-1,3,5-undecatriene, 4 and 5, were also based on a simple and convenient procedure developed recently in our laboratory for the diastereoselective synthesis of (E)-1-trimethylsilyl-3-en-1-ynes (10)[18](Scheme 3).

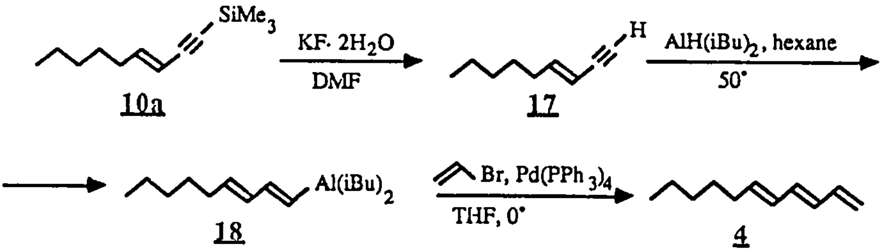
SCHEME 3



This procedure stemmed from the observation that in the stereospecific Pd-catalyzed reaction of trimethylsilylethynylzinc chloride (15), (E)-1-bromo-1-alkenes, (E)-16, react preferentially in the presence of the corresponding (Z)-stereoisomers, (Z)-16. In particular, it was found that, when treated with n equiv of 15 and 2 mole% of Pd(PPh$_3$)$_4$ in THF at 0°, a diastereoisomeric mixture of 16

which contains n equiv of (E)-16 affords in good isolated yield (75-80%) an (E)-1-trimethylsilyl-3-en-1-yne (10) having 95-98% stereoisomeric purity. According to this procedure, a stereoisomeric mixture of 1-bromo-1-heptene (16a), (E/Z = 61.4/38.6), which was prepared according to a general method to synthetize (E)/(Z)-1-brom-1-alkenes starting from the corresponding 1-alkenes[19], gave in 80.9% yield (E)-1-trimethylsilyl-3-nonen-1-yne (10a) having 97.3% stereoisomeric purity.
An improvement of the stereoisomeric purity of 10a was obtained in another preparation which was carried out under similar experimental conditions, but using a 1/1.57 molar ratio between 1-trimethylsilylethynylzinc chloride (15) and 16a (E/Z = 82.2/17.8). In this case, compound 10a, which was obtained in 76% yield, had 99% stereoisomeric purity.
Compound 10a (97.3% stereoisomeric purity) was then converted into (3E,5E)-1,3,5-undecatriene (4) according to the simple reaction sequence illustrated in Scheme 4.

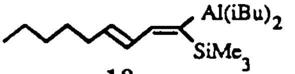
SCHEME 4



Desilylation of 10a with potassium fluoride in DMF gave in 73.7% yield (E)-3-nonen-1-yne (17) which was chemo-, regio- and stereoselectively converted into the corresponding diisobutyl-1,3-alkadienyl alane (18) by reaction with a 1 M hexane solution of diisobutylaluminum hydride at 50°. Treatment of this crude organoaluminum compound with a THF solution of vinyl bromide at 0°, in the presence of a catalytic quantity of Pd(PPh$_3$)$_4$, afforded in 50.3% yield compound 4 having 96.4% stereoisomeric purity. Compound 4 exhibited spectral properties in very good agreement with those reported for an authentic sample of (3E,5E)-1,3,5-undecatriene[10,14].

On the basis of these results, this quite short synthesis of 4 resulted superior to that based on the SO$_2$ extrusion from an (E)-alkenylsulfolene[13], which affords 4 with 83% stereoselectivity, as well to that based on the α-alkylation of a pentadienyl carbamate[10], which is more lengthy and requires the purification of an intermediate by column chromatography. It should be also noted that the above synthesis resulted more selective than that described by Ratovelomanana and Linstrumelle[15].

We next turned our attention to the preparation of (3Z,5E)-1,3,5-undecatriene (5). The key features of the devised synthetic plan included i) the construction of the terminal (3Z,5E)-trienic system present in 5 bu a Pd-catalyzed cross-coupling reaction between vinylzinc chloride and (1Z,3E)-1-iodo-1,3-nonadiene (20); ii) the preparation of 20 by a stereospecific reaction of (1Z,3E)-1-trimethylsilyl-1,3-nonadiene (19) with iodine in dichloromethane, according to the method described in the literature to prepare stereospecifically vinyl halides from the corresponding vinylsilanes[20]; iii) the selective synthesis of 19 starting from (E)-1-trimethylsilyl-3-nonen-1-yne (10a), according to a known procedure[21].



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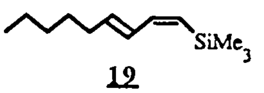

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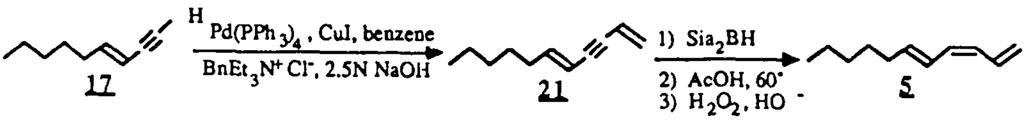
Thus, an ether solution of 10a (98% stereoisomeric purity) was reacted with diisobutylaluminum hydride to produce dienylalane 18. Hydrolysis of 18 with 3 N NaOH at 0° afforded compound 19 in 93% yield. Gas chromatography coupled with mass spectrometry showed that 19 had 95% chemical purity. However, when it was attempted to transform 19 into 20 by reacting 19 with an equimolar amount of iodine in dichloromethane at 20° in the dark, a very complex reaction mixture was obtained, also using short reaction times. Thus, this synthetic route was abandoned and another approach was investigated in which the construction of the triene system present in 5 was based on the use of (E)-3-nonen-1-yne (17) as key compound (Scheme 5).

SCHEME 5



Thus, compound 17, prepared from a sample of 10a having 99% stereoisomeric purity, was reacted with a molar excess of vinyl bromide. The reaction which was carried out at room temperature under phase transfer conditions employing benzyltriethylammonium chloride as phase-transfer agent, a large excess of 2.5 N NaOH as base, and a mixture of $Pd(PPh_3)_4$ and CuI as catalyst[22] (molar ratio Pd/Cu = 1.98), afforded in 88.6% isolated yield (E)-1,5-undecadien-3-yne (21) having 99% chemical and stereoisomeric purity. Reduction of 21 with disiamylborane, followed by protonolysis with acetic acid and treatment with 6 N NaOH and hydrogen peroxide, gave in 73% yield compound 5 having 98.6% stereoisomeric purity.

It must be noted that the present synthetic route represent s the most stereoselective synthesis of 5.

In conclusion, the Pd-catalyzed carbon-carbon bond forming reactions employed to prepare compounds 3, 4 and 5 are highly selective and afford products having very high stereoisomeric purity. Moreover, the preparative potential of the routes followed to synthetize these trienes must be emphasized since all the above syntheses were performed on multigram scale. Finally, it should be noted that these synthetic routes appear applicable to the preparation of a large array of naturally occurring substances and their derivatives bearing conjugated terminal trienic systems of (Z,E)-, (E,E)-, or (E,Z)-configuration.

EXPERIMENTAL

All boiling points are uncorrected. IR spectra were determined on a Perkin Elmer 283 B spectrophotometer. Mass spectra were recorded ona VG 70-70E mass spectrometer interfaced with a Dani 3800 gas-chromatograph. ^{1}H NMR spectra were recorded on a Varian T 60, a Varian XL 100, or a Varian VXR 300 spectrometer, using TMS as an internal standard. UV spectra were recorded on a Jasco Uvidec 710 spectrometer. GLC analyses were performed on a Dani 6500 gas-chromatograph equipped with a Perkin Elmer LCI integrator. Two types of capillary columns were used: a PEG-Permaphase bonded FSOT column (25 m x 0.23 mm) and a SRL-300 bonded FSOT column (30 m x 0.25 mm).

Purifications by liquid chromatography were performed on a Jobin-Yvon Chromatospac Prep-10 liquid chromatograph, using a Knauer differential refractometer as detector.

All reactions of air and water sensitive materials were performed in flame dried glassware under argon or nitrogen. Air sensitive solutions were transferred with hypodermic syringes or double-ended needles. All solvents were dried by conventinal methods, freshly distilled, and degassed.

(E)-1-Bromo-3-nonyn-1-ene (9a)

1-Heptyne (9.62 g, 0.10 mol) was added to a solution of ethylmagnesium bromide (0.1 mol) in THF (130 ml). After the addition was complete heating was continued for 1 h. The solution of so obtained 1-heptynylmagnesium bromide was then slowly added with stirring to a solution of $ZnCl_2$ (15.5 g, 0.113 mol) in THF (100 ml) cooled at 0°. After cooling to - 50°, a solution of $Pd(PPh_3)_4$ (4.24 g, 3.7 mmol) and (E)/(Z)-1,2-dibromoethylene (12) (93 g, 0.50 mol, E/Z = 40/60) in THF (80 ml), which was prepared immediately prior to use, was added and the reaction mixture was stirred for 1 h at -50°, 4 h at -20°, then 12 h at 0°. 1 N Hydrochloric acid was added and the mixture was extracted with pentane. The extracts were filtered through celite, dried and concentrated at 100 Torr. The residue was purified by chromatography on a Merck H 60 silica gel column using pentane as eluant, followed by fractional distillation to give compound 9a (11.65 g) in 58% yield based on 1-heptyne. B.p. 99-99.5/9 Torr. ^{1}H NMR (60 MHz, $CDCl_3$): δ 6.50 (d, 1H, J = 14 Hz), 6.07 (dt, 1H, J = 14 and 2 Hz), 2.53-1.9 (br m, 2 H), 1.83-1.1 (br, 6 H), 0.90 ppm (t, 3 H). Found : C, 53.65; H, 6.37. Calc. for $C_9H_{13}Br$: C, 53.75; H, 6.51.
GLC analysis on a PEG-Permaphase capillary column showed that compound 9a had stereoisomeric purity higher than 97%.
Fractional distillation allowed also to recover (E)-8-hexadecen-6,10-diyne (13a) (3.8 g) in 17% yield based on 1-heptyne. B.p. 97-98°/0.04 Torr. ^{1}H NMR (60 MHz, $CDCl_3$): δ 5.88 (s, 2 H), 2.8-1.93 (br, 4 H), 1.9- 1.3 (br, 12 H), 0.90 ppm (t, 6 H). IR (neat): ν 3040, 2960, 2920, 2870, 2740, 2670, 2330, 2220, 2180, 1770, 1715, 1675, 1625, 1595, 1470, 1430, 1380, 1370, 1350, 1340, 1330, 1295, 1270, 1235, 1105, 1065, 975, 960, 935, 905, 720 cm^{-1}. MS (m/e): 216 (M^+, 77), 159 (16), 145 (37), 131 (74), 117 (74), 105 (59), 91 (100), 79 (36), 55 (45), 41 (69).
Found: C, 88.90. H, 11.21. Calc. for $C_{16}H_{24}$: C, 88.82; H, 11.18. GLC analysis on a PEG-Permaphase capillary column showed that compound 13a had stereoisomeric purity higher than 99%.

(E)-3-Undeca-1,3-dien-5-yne (14)

To a solution of $ZnCl_2$ (18.9 g, 0.139 mol) in THF (140 ml) cooled at 0° was added a 1M THF solution of vinylmagnesium bromide (135 ml, 0.135 mol). A solution of compound 9a (17.01 g, 0.084 mol) and $Pd(PPh_3)_4$ (1.96 g, 1.69 mmol) in THF (50 ml) was then transferred via stainless-steel cannula to the cold solution of vinylzinc chloride. This was stirred at room temperature for 12 h, quenched with 1 N hydrochloric acid, diluted with water, and extracted with pentane. The extracts were washed with water, dried, filtered trough celite, concentrated in vacuo and purified by chromatography on silica gel, using pentane as eluant. The collected fractions were concentrated in vacuo and fractionally distilled to give compound 14 (9.14 g) in 73% yield.
B.p. 76-77°/2.5 Torr. ^{1}H NMR (100 MHz, $CDCl_3$): δ 6.8-6.0 (m , 2 H), 5.60 (br d, 1 H , J = 14 Hz), 5.4-4.95 (m , 2 H), 2.6-2.0 (br m, 2 H), 1.9-1.1 (br, 6 H), 0.90 ppm (br t, 3 H).
IR (neat): ν 3080, 3020, 2990, 2960, 2940, 2870, 2860, 2320, 2200, 1810, 1780, 1620, 1580, 1460, 1455, 1450, 1410, 1375, 1360, 1345, 1325, 1295, 1275, 1250, 1230, 1160, 1100, 1060, 995, 930, 895, 835, 800, 775, 720, 640 cm^{-1}. Found: C, 89.01; H, 11.02. Calc. for $C_{11}H_{16}$: C, 89.12; H, 10.88.
GLC analysis on a PEG-Permaphase capillary column showed that 14 had 96% stereoisomeric purity and chemical purity higher than 99.5%.

(3E,5Z)-1,3,5-Undecatriene (3)

A THF solution of disiamylborane prepared starting from a 10 M solution of borane-dimethyl sulfide complex (6.49 ml, 64.9 mmol), 2-methyl-2-butene (14.2 ml, 134.5 mmol) and THF (70 ml) was added in 30 min to a solution of compound 14 (7.41 g, 50.0 mmol) in THF (60 ml) cooled at -10°. The solution was stirred for 4 h at 0°, then acetic acid (18.2 ml) was added and the mixture was heated at 60° for 6 h under stirring. After cooling to room temperature, 6 N NaOH (100 ml, 0.60 mol) was added, followed by addition of 35% hydrogen peroxide (21 ml), maintaining the temperature below 40°. The mixture was cooled to room temperature, diluted with water saturated with NaCl and extracted with pentane. The extracts were washed with water, dried, concentrated in vacuo and purified by chromatography on silica gel, using pentane as eluant.
The collected fractions eluted were concentrated and fractionally distilled to give compound 3 (5.62 g) in 75% yield. B.p. 67°/2.3 Torr. (Lit^{15} b.p. 65°/3 Torr).
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.53-6.28 (m, 2 H), 6.16 (dd, 1 H, J = 15.2 and 11 Hz), 5.98 (br t, 1 H, J = 11 Hz), 5.45 (d t, 1 H, J = 10.8 and 8.3 Hz), 5.17 (d, 1 H, J = 16.5 Hz), 5.04 (d, 1 H J = 10.1 Hz), 2.2-2.08 (m, 2 H), 1.42-1.08 (br m, 6 H), 0.86 ppm (t, 3 H).

IR (neat): ν 3100, 3020,2960, 2930, 2880, 2860, 1870, 1800, 1720, 1650, 1560, 1395, 1380, 1370, 1345, 1325, 1290, 1240, 1175, 1125, 1105, 1025, 1005, 935, 895, 840, 740 cm^{-1}.
MS (m/e): 150 (M^+, 30), 93 (25), 91 (25), 82 (9), 80 (69), 79 (100), 77 (15), 76 (33), 67 (14), 66 (10), 65 (8), 41 (17).
GLC analysis on a PEG-Permaphase capillary column showed that compound 3 had 97.6%chemical purity and 98.2% stereoisomeric purity.
The spectral properties of 3 were in good agreement with those previously reported[14].

(E)/(Z)-1-Bromo-1-heptene (16a)

To a solution of 1-heptene (35.05 g, 0.357 mol) in dichloromethane (175 ml) cooled at -60° was slowly added bromine (18.35 ml, 0.36 mol). The mixture was stirred at -60° for 0.5 h,then it was warmed to room temperature and washed with a saturated aqueous solution of $NaHCO_3$ and water.
It was then dried and concentrated in vacuo. A suspension of the residue (88 g) in petroleum ether (b.p.>250°) (370 ml) and Aliquat 336 (3.41 g) was added to powdered potassium hydroxide (23.73 g, 0.423 mol). The mixture was maintained at 85° for 3 h, then further powdered potassium hydroxide (5.5 g, 96 mmol) was added. After 3 h at 85° the reaction products were distilled directly out of the reation mixture at 5 Torr. The distillate was dried and fractionally distilled through a Micro-Spaltrohr column to give (E)/(Z)-1-bromo-1-heptene (16a) (28.6 g) in 33% yield based on 1-heptyne. B.p. 88-91°/52 Torr.
^1H NMR (100 MHz, $CDCl_3$): δ 6.5-5.7 (m, 2 H), 2.6-1.8 (br, 2 H), 1.8-1.5 (br, 6 H), 0.90 ppm (t, 3 H). Found: C, 47.69; H, 7.50. Calc. for $C_7H_{13}Br$: C, 47.49; H, 7.40.

(E)-1-Trimethylsilyl-3-nonen-1-yne (10a)

Trimethylsilylacetylene (7.55 g, 77 mmol) was added to a solution of ethylmagnesium bromide (77 mmol) in THF (110 ml). After the addition was complete, heating was continued for 1 h. The THF solution was then added to an ice-cooled solution of $ZnCl_2$ (10.5 g, 77 mmol) in THF (75 ml) and the resulting mixture was stirred for 0.5 h at 0°. A degassed solution of (E)/(Z)-1-bromo-1-heptene (16a) (28.83 g, 0.162 mol, E/Z = 61.4/38.6) and $Pd(PPh_3)_4$ (2.37 g, 2.05 mmol) in THF (65 ml) which was prepared immediately prior to use, was added to this reaction mixture which was maintained at 0° for 5.5 h under stirring. After this period the reaction was quenched by adding 1 N hydrochloric acid at 0°. The reaction mixture was diluted with water and extracted with hexane. The organic layer was washed with water, fltered trough celite, dried and concentrated in vacuo. The residue was purified by chromatography on silica gel using hexane as eluant, followed by fractional distillation to give compound 10a (12.71 g) in 80.9% yield. B.p. 85.5-86°/1.7 Torr.
^1H NMR (60 MHz, CCl_4): δ 6.17 (dt, 1 H, J= 16 and 7 Hz), 5.41 (dm, 1 H, J= 16 Hz), 2.07 (br t, 2 H), 1.63-1.1 (br, 6 H), 0.93 (br t, 3 H), 0.15 ppm (s, 9H).
IR (neat): ν 3025, 2860, 2800, 2760, 2140, 2070, 1465, 1440, 1410, 1380, 1300, 1250, 1085, 955, 840, 760, 725 cm^{-1}.
MS (m/e): 194 (M^+, 10), 180 (16), 179 (M^+-15, 100), 122 (5), 109 (12), 107 (5), 84 (5), 73 (13), 59 (12), 43 (6).
Found: C, 74.45; H, 11.27. Calc. for $C_{12}H_{22}Si$: C, 74.14; H, 11.41.
GLC analysis on a PEG-Permaphase capillary column showed that compound 10a had 97.3% stereoisomeric purity.
Another preparation of compound 10a was carried out under similar experimental conditions, but using a 1/1.57 molar ratio between trimethylsilylacetylene and (E)/(Z)-1-bromo-1-heptene (16a)(E/Z = 82.2/17.8). Compound 10a which was obtained in 76% yield, had 99% stereoisomeric purity.

(E)-3-Nonen-1-yne (17)

Potassium fluoride dihydrate (10.87 g, 0.115 mol) was added to a solution of compound 10a (97% stereoisomeric purity) (11.7 g, 60 mmol) in DMF (40 ml). The resulting mixture was stirred for 2 h at 20°, treated with 3 N hydrochloric acid (500 ml) and extracted with pentane. The extracts were washed with water, dried , concentrated and fractionally distilled to give compound 17 (5.48 g) in

73.7 % yield. B.p. 91.5-92°/90 Torr.
^{1}H NMR (60 MHz, CCl$_4$) : δ 6.17 (dt, 1 H, J= 16 and 7 Hz), 5.35 (dm, 1 H, J= 16 Hz), 2.58 (d, 1 H), 2.43-1.76 (br t, 2 H), 1.67-1.03 (br, 6 H), 0.87 ppm (br t, 3 H).
Found: C, 88.60; H, 11.71. Calc. for C_9H_{14}: C, 88.45; H, 11.55.
GLC analysis on a PEG-Permaphase capillary column showed that compound 17 had stereoisomeric purity higher than 97%.

(3E,5E)-1,3,5-Undecatriene (4)

A 1 M hexane solution of diisobutylaluminum hydride (42.5 ml, 42.5 mmol) was slowly added to a solution of compound 17 (5.18 g, 42.5 mmol) (97% stereoisomeric purity) in hexane (5 ml). The mixture was stirred for 15 min at room temperature, then maintained at 48° for 5 h. This solution was then added to a solution of vinyl bromide (18.2 g, 0.17 mol) and Pd(PPh$_3$)$_4$ (1.47 g, 1.27 mmol) in THF (65 ml) cooled at 0°. The mixture was maintained at room temperature for 17 h under stirring, hydrolyzed with 10 N hydrochloric acid (30 ml), and extracted with pentane. The extracts were washed with water, filtered, dried and concentrated in vacuo. The residue was purified by chromatography on silica gel, using pentane as eluant, followed by fractional distillation to give compound 4 (3.21 g) in 50.3% yield. B.p. 63°/2.2 Torr. (Lit[15] b.p. 51°/2 Torr).
^{1}H NMR (300 MHz, CDCl$_3$): δ 6.35 (dt, 1 H, J= 16.8 and 10.1 Hz), 6.21 (dd, 1 H, J= 15.0 and 10.0 Hz), 6.12 (dd, 1 H, J= 15.0 and 10.0 Hz), 6.07 (ddt, 1 H, J= 14.8, 10.1 and 1.4 Hz), 5.73 (dt, 1 H, J= 14.8 and 7.4 Hz), 5.17 (dd, 1 H, J= 16.8 and 1.6 Hz),5.04 (dd, 1 H, J=10.1 and 1.6 Hz), 2.16-2.06 (m, 2 H), 1.46-1.22 (br m, 6 H),0.90 ppm (t, 3 H, J= 6.9 Hz).
IR (neat): ν 3080, 3020, 2960, 2870, 2850, 1790, 1640, 1625, 1585, 1465, 1455, 1430, 1410, 1375, 1360, 1330, 1275, 1185, 1130, 1110, 1095, 1000; 965, 890, 865, 835, 720,and 635 cm^{-1}.
UV (3-methylpentane): λ_{max} (ε) 273.5 (36,970), 262.5 (46,380), 253 (33,650), 245 (shoulder, 19,290).
GLC analysis on a PEG-Permaphase capillary column showed that compound 4 had 96.4% stereoisomeric purity.
The spectral properties of 4 were in good agreement with those previously reported[10,14].

(1Z,3E)-1-Trimethylsilyl-1,3-nonadiene (19)

To a solution of (E)-1-trimethylsilyl-3-nonen-1-yne (10a) (98% stereoisomeric purity) (15.59 g, 80.3 mmol) in ether (40 ml) at 25° was added neat diisobutylaluminum hydride (8.03 ml, 44.2 mmol). The mixture was heated at 40° for 4 h, the cooled to room temperature and slowly poured into ice-cold 3 N NaOH (450 ml). After extraction with hexane, the combined organic phases were successively washed with 3 N NaOH and saturated aqueous solution of NaCl and dried. Fractional distillation afforded compound 19 (14.6 g) in 93.3% yield. B.p. 78°/2.3 Torr.
^{1}H NMR (60 MHz, CDCl$_3$): δ 7.0-5.25 (m, 4 H), 2.35-1.80 (br m, 2 H), 1.7-1.0 (br m, 6 H), 0.90 (br t, 3 H), 0.20 ppm (s, 9 H).
IR (neat): ν 3010, 2910, 2870, 2860, 1640, 1565, 1460, 1410, 1380, 1300, 1240, 1055, 1035, 990, 830, 750, 720, 680, 670 cm^{-1}.
MS (m/e): 196 (M$^+$, 13.3), 181 (38.7), 126 (14), 125 (23), 112 (12), 111 (26.7), 73 (55) 59 (100), 45 (11.3), 43 (10).
Found: C, 73.67; H, 12.16. Calc. for $C_{12}H_{24}Si$: C, 73.38; H, 12.32.
GLC analysis on a PEG Permaphase capillary column showed that compound 19 had 96.4% stereoisomeric purity.

(E)-1,5-Undecadien-3-yne (21)

A degassed solution of vinyl bromide (27.8 g, 0.26 mol) in benzene (60 ml) was added under argon to a mixture of benzyltriethylammonium chloride (0.488 g, 2.28 mmol), cuprous iodide (0.744 g, 3.91 mmol) and Pd(PPh$_3$)$_4$ (2.27 g, 1.97 mmol). To this mixture cooled at 0° was added compound 17 (99% stereoisomeric purity) (7.96 g, 65.2 mmol) and a deareated 2.5 N aqueous solution of NaOH (118 ml, 0.295 mol), and the resulting mixture was stirred at room temperature for 16 h. It was then treated with saturated NH$_4$Cl solution and extracted with hexane. The extracts were washed with saturated NH$_4$Cl solution and water until neutrality. After filtering through celite, drying and concen-

tration in vacuo, the residue was diluted with pentane and filtered. The filtrate was concentrated and purified by chromatography on silica gel, using pentane as eluant, followed by fractional distillation to give compound 21 (7.88 g) in 88.6% yield. B.p. 79–80°/4 Torr.
^{1}H NMR (300 MHz, CDCl$_3$): δ 6.15 (dt, 1 H, J= 15.7 and 7.2 Hz), 5.84 (ddd, 1 H, J= 17.5, 11.1 and 2.1 Hz), 5.64–5.51 (m, 2 H), 5.43 (dd, 1 H, J= 11.1 and 2.2 Hz), 2.17–2.05 (m, 2 H), 1.47–1.34 (m, 2 H), 1.34–1.20 (m, 4 H), 0.90 ppm (t, 3 H, J= 6.8 Hz).
IR (neat): ν 3100, 3030, 3020, 2860, 2830, 2780, 2760, 2190, 1830, 1630, 1605, 1585, 1470, 1460, 1415, 1380, 1290, 1185, 970, 950, 910, 725, and 670 cm^{-1}.
MS (m/e): 148 (M$^+$, 25), 105 (10), 91 (47), 78 (100), 65 (19), 51 (8), 41 (15).
Found: C, 89.10; H, 10.91. Calc. for C$_{11}$H$_{16}$: C, 89.12; H, 10.88.
GLC analysis on a SRL-300 capillary column showed that compound 21 had 99% chemical and stereoisomeric purity.

(3Z,5E)-1,3,5-Undecatriene (5)

Reduction of compound 21 (7.15 g, 48.3 mmol) with disiamylborane, according to a procedure similar to thet employed to convert compound 14 into triene 3, afforded (3Z,5E)-1,3,5-undecatriene (5) (5.3 g) in 73.1% yield. B.p. 68°/2 Torr.
^{1}H NMR (300 MHz, CCl$_4$): δ 6.72 (dt, 1 H, J= 16.7 and 10.1 Hz), 6.41 (br dd, 1 H, J= 15.0 and 10.0 Hz), 5.98–5.74 (m, 2 H), 5.65 (dt, 1 H, J= 14.9 and 7.3 Hz), 5.12 (dd, 1 H, J= 16.7 and 1.8 Hz), 5.04 (br d, 1 H, J= 10.0 Hz), 2.18–2.02 (br m, 2 H), 1.50–1.20 (br m, 6 H), 0.90 ppm (t, 3 H).
IR (neat): ν 3090, 3030, 3010, 2990, 2960, 2930, 2875, 2860, 1800, 1640, 1620, 1465, 1455, 1440, 1380, 990, 970, 940, 850, 820, 785, 725, 640 cm^{-1}.
UV (hexane): λ_{max} (ε) 277 (29,670), 262 (40,030), 253 (31,720), 245 (shoulder, 20,220), 200 nm (3,880).
MS (m/e): 150 (M$^+$, 10.7), 94 (4.7), 93 (4.7), 91 (5.3), 80 (12.7), 79 (100), 77 (14), 41 (6).
GLC analysis on a SRL-300 capillary column showed that compound 5 had 98.6% stereoisomeric purity. The spectral properties of 5 were in good agreement with those previously reported[3c,14].

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