DIENIC SEX PHEROMONES

STEREOSELECTIVE SYNTHESES OF (7E,9Z)-7,9-DODECADIEN-1-YL ACETATE, (E)-9,11-DODECADIEN-1-YL ACETATE, AND OF (9Z, 11E)-9,11-TETRADECADIEN-1-YL ACETATE BY PALLADIUM-CATALYZED REACTIONS[a]

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(*Received in UK 25 November 1980*)

Abstract—Pure (7E,9Z-7, 9-dodecadien-1-yl acetate (**1**), the sex pheromone of *Lobesia botrana*, has been prepared in 21.6% overall yield by a reaction scheme involving; (i) the cross-coupling of (*E*) - 8 - (2 - tetrahydropyranyloxy) - 1 - octenyldisiamylborane with 1 - bromo - 1 - butyne, in the presence of a Pd (O) catalyst and base; (ii) the acetylation of the crude product of this reaction; (iii) the (*Z*)-stereoselective reduction of the obtained conjugated (*E*)-enyn-1-yl acetate.

(*E*)-9, 11-Dodecadien-1-yl acetate (**2**), a sex pheromone component of *Diparopsis castanea*, has been analogously obtained (in 54.3% overall yield) by cross-coupling of (*E*) - 10 - (2 - tetrahydropyranyloxy) - 1 - decenyl borane with vinyl bromide, in the presence of a Pd (O) catalyst and base, followed by acetylation of the crude product. Compound **2**, which was 87.7% chemically pure, was purified by column chromatography over SiO_2–$AgNO_3$. Chemically pure (9Z, 11E) - 9,11 - tetradecadien - 1 - yl acetate (**3**), a sex pheromone component of *Spodoptera littoralis*, has been prepared (in 30.2% overall yield) by reaction of 10 - (2 - tetrahydropyranyloxy) - 1 - decynylmagnesium bromide with (*E*)-1-iodo-1-butene, in the presence of a Pd (O) catalyst, followed by acetylation of the crude product and by (*Z*)-stereoselective reduction of the obtained (*E*)-enyn-1-yl acetate.

The stereoisomeric purity of **1**, **2** and **3** has been evaluated by glc analysis on glass capillary columns or by reverse phase hplc analysis.

Sex pheromones of insects belonging to the order of Lepidoptera include several diunsaturated conjugated compounds differing either in the chain lengths, or in the positions and configuration of their double bonds.[1-3] Rather common are (*Z*, *E*)- or (*E*, *Z*)-dienic systems which are present, in the pheromones of *Lobesia botrana*,[4] *Spodoptera littoralis*,[5] *Bombyx mori*,[6] *Dendrolimus punctatus*,[7] and of *Prionoxystus robinae*.[8] On the other hand, conjugated (*E*, *E*)- and (*Z*, *Z*)-double bonds are present in the sex pheromones of *Laspeyresia pomonella*[9] and of *Amyelois transitiella*,[10] respectively. On the contrary, a component of the sex pheromone of *Diparopsis castanea* represents, to our knowledge the only example of a terminal conjugated (*E*)-diene system.[5]

Large numbers of methods for the synthesis of conjugated dienic sex pheromones have been previously developed and discussed in review articles.[1-3, 11] More recent progress in this area has been made through the development of methods involving the synthesis of (*Z*, *E*)- or (*E*, *Z*)-1,3-dienes (i) by stereospecific coupling of (*Z*, *E*) - 2,4 - dien - 1 - aminium salts with Grignard reagents in the presence of dilithium tetrachloro cuprate,[12, 13] (ii) by stereoselective rearrangement of silyl

ketene acetals of 1-alkynyl-2-propenyl acetates, followed by *Z*-stereo-selective reduction,[14] (iii) by Pd catalyzed decarboxylative elimination of adducts from enals and carboxylate enolates,[15] (iv) or by alkylation of alkynyl Cu(I) derivatives with 1 - halo - 1 - alkynes followed by stereoselective reduction of the functionalized enynes.[16]

On the other hand the synthesis of functionalized (*E*, *E*) - 1,3 - dienes has been recently achieved by stereospecific coupling (i) of (*E*) - 1 - alkenyldisiamyl boranes with (*E*) - 1 - alkenyl halides in the presence of a Pd catalyst and base,[17] or (ii) of (*E*) - 1 - alkenyl-magnesium bromides with (*E*)-alkenyl iodides in the presence of tetrakis(triphenylphosphine)palladium.[18] Finally, (*Z*, *Z*)-1, 3-dienes have been obtained either by a route involving a Cadiot–Chodkiewicz coupling reaction and a dialkylborane reduction,[19] or by a sequence of reactions involving the coupling of 1 - alkynyl - 2 - propenyl acetates with alkylmagnesium halides, in the presence of a Cu(I) catalyst, followed by (*Z*)-stereoselective reduction of the obtained conjugated enynes.[14]

We now wish to report new and expeditious methods for the stereoselective synthesis of (7E,9Z) - 7,9 - dodecadien - 1 - yl acetate (**1**), the sex pheromone of the European grape vine moth,[4, 20] *Lobesia botrana* (Denis et Schiff), of (*E*) - 9,11 - dodecadien - 1 - yl acetate (**2**), a sex pheromone component of the red bollworm moth,[5, 21] *Diparopsis castanea* (Hamps), and of (9Z, 11E) - 9,11 -

tetradecadien - 1 - yl acetate (3), a sex pheromone component of the Egyptian cotton leafworm,[5,22] *Spodoptera littoralis* (Boisd.).

The construction of the dienic systems, present in 1 and 2, was quite different from the previous synthetic approaches[20,21] and was carried out according to a

recently described general method for the synthesis either of conjugated (*E*)-enynes,[17,23] or of conjugated (*E, Z*)-dienes[17] (Schemes 1 and 2). Such method involves the stereospecific cross-coupling of (*E*) - 1 - alkenyl-disiamylboranes with 1-alkynyl halides or 1-alkenyl halides, in the presence of a catalytic amount of
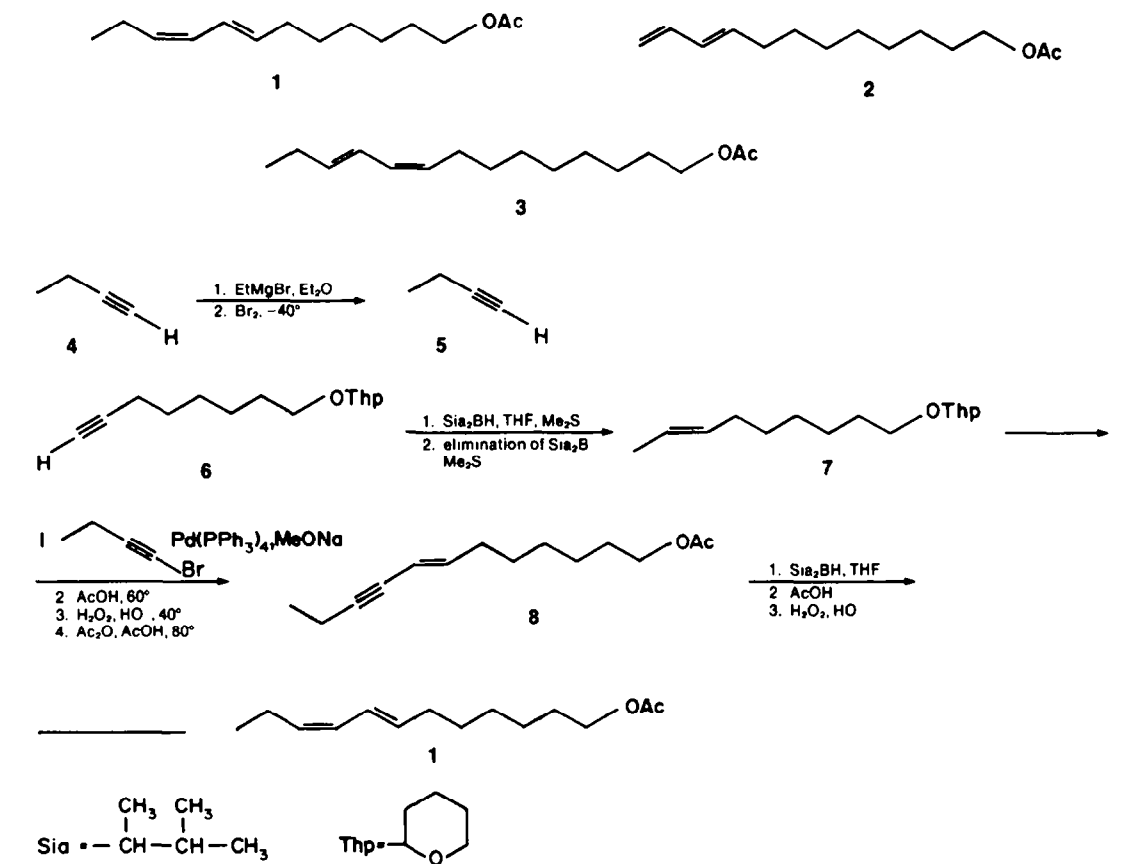
Scheme 1.
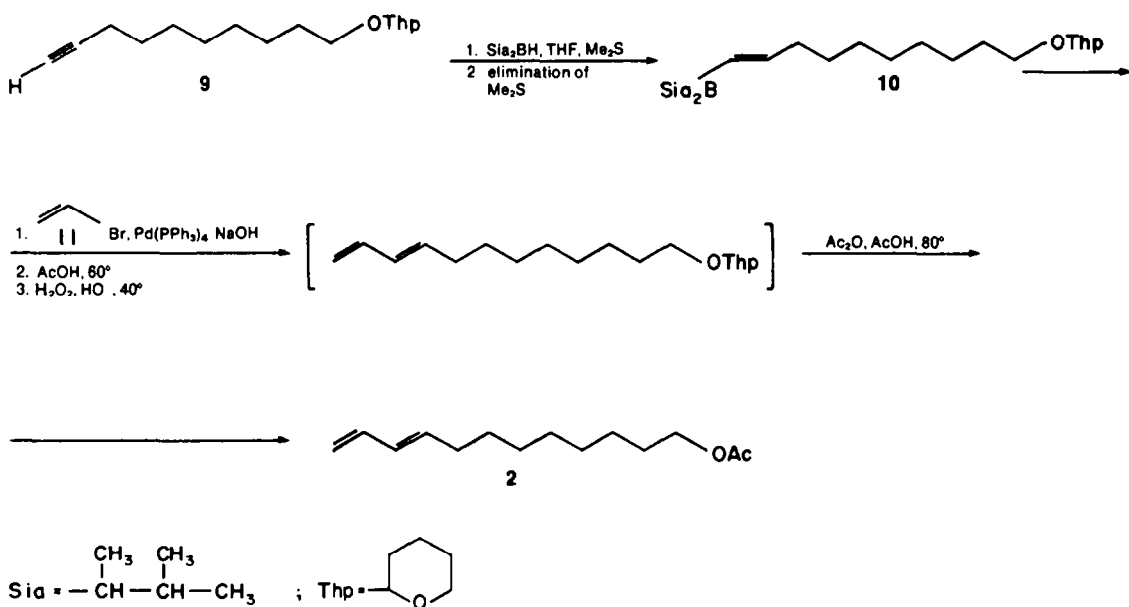
Scheme 2.

tetrakis(triphenylphosphine)palladium and base.[17] On the contrary, (Z,E)-diene **3** was obtained by a reaction sequence (Scheme 3) in which the corresponding (E)-enyne system was constructed by a general method involving the cross-coupling of an 1-alkynylmagnesium halides with an (E) - 1 - alkenyl iodide, in the presence of tetrakis(triphenylphosphine)palladium.[18]

Synthesis of the European grape vine moth pheromone **1**. The synthesis of **1** was carried out by the sequence of reactions depicted in Scheme 1, in which 1-bromo - 1 - butyne (**5**) and 1 - (2 - tetrahydropyranyloxy) - 7 - octyne (**6**) were used as key compounds.

1-Butyne (**4**) was converted into 1-butynylmagnesium bromide, which was reacted in ether at −40° with 0.85 equivalents of bromine to give **5** in 50% overall yield. Compound **6**, which was obtained in 82% yield starting from 1 - (2 - tetrahydropyranyloxy) - 6 - chlorohexane and lithium acetylide–ethylenediamine complex,[24] was reacted with disiamylborane in THF at 20° for 4 hr. (E)-**8** - (2 - Tetrahydropyranyloxy) - 1 - octenyldisiamyl-borane (**7**) so obtained was then treated sequentially with a benzene solution of 0.9 equivalents of **7**, containing a catalytic quantity of tetrakis(triphenyl-phospine)palladium, and with 2 equivalents of sodium methoxide in methanol. After refluxing for 2 hr, the residual organoborane was decomposed by reaction at first with acetic acid, subsequently with 6N NaOH and 36% H_2O_2, and the product was extracted with ether. Treatment of this crude product with acetic anydride and acetic acid gave enyne **8** which was simply isolated (48% yield) by distillation through a Vigreux column. Glc analysis on a high resolution glass capillary column (Carbowax 20 M) showed that **8** had 98.3% chemical

purity and 99% stereoisomeric purity. Treatment of **8** and disiamylborane, followed by protonolysis and reaction with hydrogen peroxide afforded diene **1** in 90% yield. Such compound, which was characterized by ^{1}H NMR, ^{13}C NMR, UV, IR and mass spectroscopy, exihibited spectral properties identical with those of an authentic sample prepared according to Negishi and Abramovitch.[20c] Glc and hplc analyses showed that **1** had chemical purity higher than 99% and was 97.6% stereoisomerically pure.

Taking into account these results, the above synthesis resulted to be much more convenient than others previously reported in which it is necessary to purify some intermediates by fractional crystallization,[20a, b, c, f] or in which the final product results stereoisomerically impure.[13, 20b, c] Moreover, it seemed adaptable for the preparation either of **1** on a large scale, or of other conjugated (E, Z)-dienes containing functional groups.

Synthesis of the red bolloworm moth pheromone component **2**. Next, we attempted to synthesize the terminal conjugated dienic pheromone component **2**, using a scheme utilizing a readily obtainable (E)-1-al-kenylboron, and we planned to introduce the terminal double bond by cross-coupling of such organoboron with vinylbromide in the presence of tetrakis(triphenyl-phosphine)palladium and base (Scheme 2), i.e. according to the procedure employed in literature, without success, for the direct stereospecific synthesis of (E, Z)-dienes.[17] The coupling between (E)-10-(2-tetrahydropyranyloxy)-1-decenyldisiamylborane (**10**) and vinyl bromide (**11**) was carried out by dropwise addition of a THF solution of **11**, containing a catalytic quantity of tetrakis(triphenyl-phosphine)palladium, to a THF solution of **10**,[b] followed by addition of 2 equivalents of a 2N NaOH. After refluxing, the residual organoborane was decomposed by protonolysis and treatment with hydrogen peroxide. Acetylation of the crude product, followed by fractional distillation at low pressure gave pheromone **2**, in 54.3% yield. Glc analysis showed that this compound had 87.7%

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[b]In contrast to the procedure employed to prepare **8**, we used THF as the solvent, instead of benzene, owing to the insolubility of NaOHaq in this hydrocarbon. On the other hand, according to the literature,[17] it appeared preferable to use sodium hydroxide, instead of a sodium alcoholate.
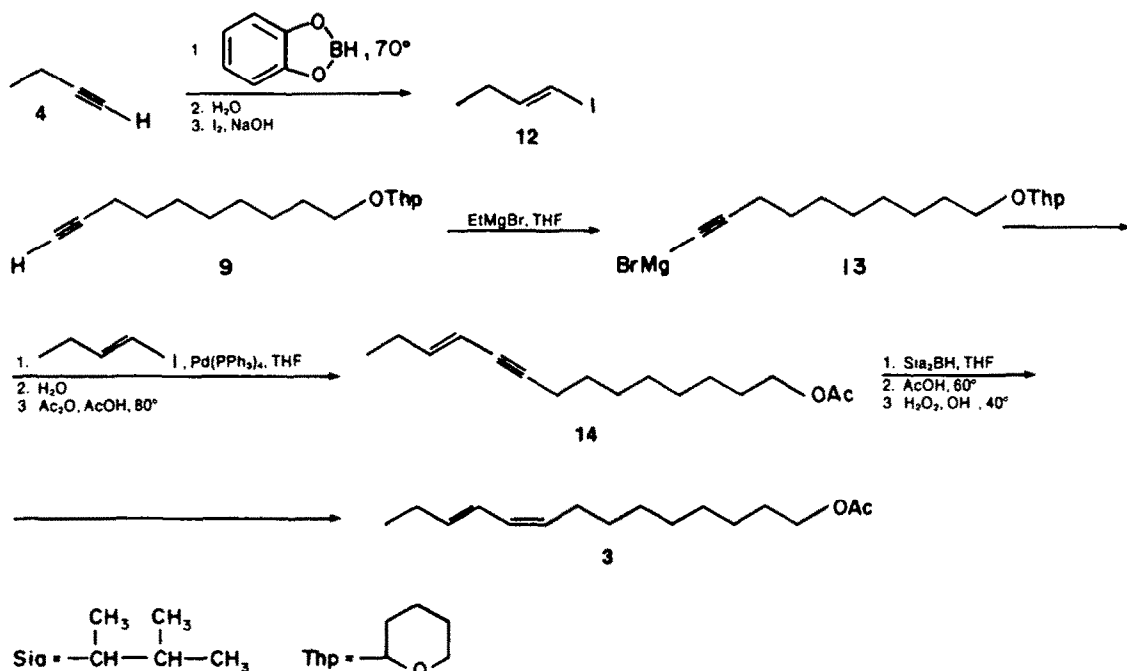
Scheme 3.

chemical purity and contained several impurities with lower and higher retention times on a Carbowax 20M glass capillary column. Thus, a small sample of this compound was purified by column chromatography over SiO_2-$AgNO_3$. The spectral properties of the purified sample (96.7%) were in good agreement with those reported for 2 in the literature.[21a–d]

Since the E and Z stereoisomers of 2 have been reported to be difficult to resolve by glc methods,[21a, c] we used a new and simple chromatographic method recently set-up in our laboratory in order to evaluate the stereoisomeric purity of the synthesized sex-pheromone component. Such method consists in the separation of the E and Z isomers of 2 by reversed-phase high performance liquid chromatography using a short column packed with octadecylsilane bounded 5μ silica particles, methanol: water (3:1) as eluent, and in the detection of such stereoisomers by their UV absorption at 232 nm.

Calibration curves were obtained using a pure sample of $(Z) - 9, 11$ - dodecadien - 1 - yl acetate and a 63:37 mixture of E and Z stereoisomers of such dienic acetate, kindly furnished us by Dr. Hall. According to this method, the stereoisomeric purity of 2 resulted to be higher than 97%[d].

On the basis of these results, the present synthesis seems to offer little improvement over other more complex syntheses of 2[21a, e, f, g] owing to the impurities present in the final product and the necessity to purify the diene before employement in field tests. However, taking into account that 2 may be easily purified by preparative hplc,[25] the present synthesis appears useful for a large scale production owing to its shortness and the satisfactory overall yield.

Synthesis of the Egyptian cotton leafworm pheromone component 3

As regards the synthesis of (Z, E)-diene 3, the cross-coupling reaction of (Z)-alkenylboranes with (E)-alkenyl halides, in the presence of a Pd catalyst and base, did not appear applicable owing to the very probable isomerization of diene 3 into the corresponding (E, E)-stereoisomer, under the Pd catalyzed reaction conditions.[17, 26] Therefore, we prepared 3 by a route (Scheme 3) involving the stereospecific construction of

conjugated (E)-enyne 14 by cross-coupling of the 1-alkynylmagnesium bromide 13 with $(E) - 1$ - iodo - 1 - butene (12), in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium. Compound 12, having stereoisomeric purity higher than 99%, was obtained in 50% yield starting from 4 by hydroboration with catecholborane, followed by hydrolysis and treatment of the obtained (E)-1-butenylboronic acid with iodine, under the influence of sodium hydroxide.[27] A benzene solution of 12 (1 equiv) was then treated sequentially with tetrakis(triphenylphosphine)palladium (0.05 equiv) and a THF solution of the Grignard reagent (1 equiv) derived from 9. The crude product was acylated to afford (E) - 11 - tetradecen - 9 - yn - 1 - yl acetate (14) in 68% yield. Treatment of 14 with disiamylborane, followed by protonolysis and reaction with hydrogen peroxide, gave, after fractional distillation of the crude product, diene 3 in 89% yield. Glc analysis showed that 3 was 99% chemically pure and had 98.7% stereoisomeric purity.

Thus, this stereoselective synthesis of 3 is superior to the methods based on Wittig reactions[20e, 22b, c, d] or on acetylenic routes.[22e] In fact, our method afforded the desired diene in high chemical and stereoisomeric purity and in satisfactory overall yield (30.2%) without purification of intermediates by fractional crystallization, or the separation of the stereoisomers of 3 by chromatography.

It was also possible to confirm qualitatively the high stereoisomeric purity of the synthesized sex pheromone components 1, 2, and 3 by examination of their ^{13}C NMR spectra. In fact, according to the reports for monoene systems,[28] or a variety of diene systems,[14] it was found that the allylic carbons present in 1, 2 and 3 have different chemical shifts dependent on the configuration of the adjacent C=C double bonds. In particular, carbons in allylic position to E- or Z- double bonds are shifted *ca* 2.7 ppm downfield and *ca* 2.5 ppm upfield, respectively with respect to analogous carbons in the corresponding saturated compounds.[28, 29] Thus, it was assumed that the absence in the ^{13}C NMR spectra of 1, 2, and 3 of signals attributable to the presence of the corresponding stereoisomers was an index of their stereoisomeric purity.[e]

In conclusion, the above reactions provide two general methods for the highly regio-, chemo- and stereoselective synthesis of functional E, Z- and Z, E dienes. It is our opinion that these methods allow large scale preparations of the desired dienes.

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[c] Recently it has been reported that the direct separation of the stereoisomers of 9, 11 - dodecadiene - 1 - yl acetate may be accomplished by glc using a nematic liquid crystal, 4 - (*p* - methoxycinnamyloxy) - 4' - methoxyazobenzene, as stationary phase. [R. Lester and D. R. Hall, *J. Chromat.* **190**, 35 (1980)].

[d] Glc analysis on a 1.8 m × 2 mm i.d. glass column packed with 5% 4 - (*p* - methoxycinnamyloxy) - 4' - methoxyazobenzene on 100–200 mesh GasChrom Q (temp. programmed from 120° at 1°/min) showed that 2 contained the Z and E-isomers in 2.4:97.6 ratio. Such analysis was carried out by Miss M. Eyles in the laboratory of Dr. R. Hall at the Tropical Product Institute (London).

[e] A quantitative evaluation of the stereoisomeric purity of such compounds could not be given in this case since, owing to the decoupling technique used, the C atoms of a same molecule had, very probably, different Overhauser nuclear effect. We now are attempting to set up a method for the quantitative ^{13}C NMR analysis of the stereoisomeric purity of monoenic and dienic pheromones. Such method is based on the use of Cr(III) acetylacetonate to eliminate the Overhauser nuclear effect [J. N. Shoolery, W. C. Jankowski, *Applications Note* N.4 Varian Assoc., Palo Alto, Calif., 1975].

column packed with octadecylsilane bounded 5 micron. (SC-01) silica particles, an UV detector (232 nm), and a methanol:water (3:1) mixture as eluent.

1-Bromo-1-butyne (5)

According to the literature,[30] 1-butyne (16.2 g, 0.30 mol) reacted with a 1 M ether soln of EtMgBr to give 1-butynylmagnesium bromide. Br_2 (13 ml, 0.25 mol) was then slowly added to the ether soln of the Grignard reagent cooled at −40°. The yellow mixture was stirred for 5 min at −40°, and after the temp. was allowed to rise to room temp. it was poured into ice-water and extracted with 4 portions (50 ml) ether. Fractional distillation of the dried ether extracts gave 5 (20 g, 50% yield) b.p. 90–91°. (Lit.[31] b.p. 91°; n_D^{23} 1.5247).

Tetrakis (triphenylphosphine) palladium

This was prepared in 95% yield[32] starting from palladium dichloride, triphenylphosphine and hydrazine hydrate.

1-(2-Tetrahydropyranyloxy)-7-octyne (6)

This was prepared in 82% by reaction of 1 - (2 - tetrahydropyranyloxy) - 6 - chloro - hexane with lithium acetylide-ethylenediamine complex in DMSO.[24]

Compound 6 had: b.p. 78.5 − 79°/0.4 torr; n_D^{25} 1.4598. ^{1}H NMR (60 MHz, CCl_4). δ 4.50 (1H, br), 3.76 (2H, m), 3.47 (2H, t),2.21 (2H, br), 2.02 (2H, m), 1.83 (1H, t), 1.60 (4H, br), and 1.50 ppm (8H, br). (Found: C, 74.00; H, 10.48. Calc. for $C_{13}H_{22}O_2$: C, 74.20; H, 10.54%).

(E)-7-Dodecen-9-yn-1-yl acetate (8)

Pure 2-methyl-2-butene (0.239 mol) was slowly added to a 2M THF soln of borane–methylsulfide complex (0.115 mol) in THF (57 ml) cooled at −25°. The mixture was stirred for 2 hr at room temp, then it was added dropwise to a soln of 6 (21 g, 0.10 mol) in THF (30 ml), cooled at −10°. The resulting mixture was stirred for 4 hr at room temp. After evaporation of the volatile substances (25°/15 torr, 0.5 hr), THF (50 ml) was added. 5 (12 g, 0.09 mol) was added to a soln of tetrakis(triphenylphosphine)palladium (1.04 g. 0.9 mmol) in benzene (180 ml). After the mixture was stirred for 0.5 hr at room temp, the THF soln of 7 was added, followed by addition of a 2 M NaOMe (0.18 mol) in MeOH. The mixture was heated for 2 hr at 70°. After 10 min of heating the mixture became heterogeneus. It was then cooled at room temp, AcOH (0.3 mol) was added, and the resulting mixture was heated under stirring for 6 hr at 60°. After cooling at room temp, 6N NaOH (0.57 mol) was added, followed by addition of 36% H_2O_2 (added dropwise) (27 ml) maintaining the temp. below 40°. It was further stirred for 40 min at 40°. The mixture was then cooled and filtered. Water was added to the filtrate and the aqueous layer was saturated with NaCl. The organic layer was separated and the aqueous phase was extracted with four portions (50 ml) of ether. The combined ether extracts were washed twice with sat NaCl aq, dried over Na_2SO_4 and concentrated. The residue (26.8 g) was then reacted at 80° for 20 hr with AcOH (110 ml) and Ac_2O (50 ml). The mixture was then poured into ice-water and extracted with ether. The ether extracts were neutralized with $NaHCO_3$ aq, washed with sat NaCl aq, dried and concentrated. The residue was fractionally distilled to give (E) 8 (10.58 g, 47.6% yield based on 5) b.p. 96–97°/0.05 torr; n_D^{25} 1.4742; $ν_{max}$ 3020, 2980, 2930, 2850, 2210, 1735, 1450, 1430, 1385, 1365, 1320, 1240, 1160, 1150, 1030, 955, 885, 780, 730 and 630 cm^{-1}. ^{1}H NMR (60 MHz, CCl_4): δ 6.2–5.2 (m, 2H), 3.97 (t, 2H), 2.6–1.8 (m, 4H), 1.93 (s, 3H), 1.8–1.3 (br, 8H), and 1.13 ppm (t, 3H). ^{1}H NMR (100 MHz, $CDCl_3$): δ 6.03–5.88 (1H, sext), 5.43 (1H, d, J = 15Hz), 4.04 (2H, t), 2.50–2.0 (4H, m), 2.03 (s, 3H), 2.0–1.2 (8H, m), and 1.14 ppm (3H, t). ^{13}C-NMR: δ 13.02, 13.98, 20.89, 25.78, 28.58, 28.70, 32.80, 64.40, 78.42, 89.87, 110.01, 142.69, 170.77. Mass spectrum: m/e 222 (M$^+$), 179 (M$^+$–CH_3CO), 162 (M$^+$–CH_3COOH), 133, 119, 93, 91, 79, 77, 61 (CH_3COOH$_2^+$), 41. Glc analysis (column at 170°, t_r = 11.0 min) showed that 8 had 98.3% chemical purity and at least 99% stereoisomeric purity. Lit^{20d}: b.p. 108/0.1 torr; ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.15 (t, 2H), 2.04 (s, 3H), 2.26 (9.2H), 4.04 (t, 2H), 5.42 (d, 1H), 6.05 (sext, 1H).

(7E, 9Z)-7,9-Dodecadien-1-yl acetate (1)

A THF soln of disiamylborane, which was prepared starting from a THF soln of borane-methyl sulfide complex (45.2 mmol), 2-methyl-2-butene (93.6 mmol) and THF (25 ml), was slowly added to a soln of 8 (34.8 mmol) in THF (11 ml) cooled at −10°. The mixture was stirred for 4 hr at 0°, then AcOH (10.4 ml) was added and the resulting mixture was heated under stirring for 6 hr at 60°. After evaporation of the volatile substances (25°/15 torr, 0.5 hr), 6 N NaOH (0.344 mol) was added, followed by addition of 36% H_2O_2 (12.8 ml), maintaining the temp. below 40°. It was further stirred for 40 min at 40°. The mixture was then cooled to room temp, water was added and the aqueous layer was saturated with NaCl. The organic layer was separated and the aq layer was extracted with four portions (50 ml) of ether. The combined ether extracts were washed twice with sat NaCl aq, dried, concentrated, and fractionally distilled to give 1 in 90% yield: b.p. 88°/0.33 torr, n_D^{25} 1.4709; $ν_{max}$ 3010, 2960, 2920, 2850, 1740, 1645, 1620, 1450, 1430, 1410, 1380, 1360, 1230, 1030, 975, 940, 830, 790, and 720 cm^{-1}. ^{1}H NMR (100 MHz, $CDCl_3$): δ 6.5–5–1 (m, 4H), 2.04 (s, 3H), 1.8–1.2 (br, 8H), 0.98 ppm (3H, t). ^{13}C NMR: 14.31, 20.91, 21.01, 25.80, 28.59, 28.82, 29.26, 32.73, 64.46, 125.58, 127.88, 131.49, 134.09, 170.80. UV (heptane): $λ_{max}$ (ε) 233 nm (33641). Mass spectrum: m/e 224 (26%), (M$^+$), 164 (13%)(M$^+$–CH_3COOH), 135(22%), 121 (27%), 95 (48%), 79 (78%), 67 (100%), 61 (2%) (CH_3COOH$_2^+$). (Found: C, 74.74; H, 10.9%. Calc. for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78%). Glc analysis (column at 160° tr = 7.8 min), showed that 1 had 98.9% chemical purity and 97.6% stereoisomeric purity.

1-(2-Tetrahydropyranyloxy)-9-decyne (9)

Such compound [b.p. 95–96°/0.05 torr; n_D^{25} 1.4597] was prepared in 70% yield by reaction of 1 - (2 - tetrahydropyranyloxy) - 8 - bromooctane with lithium acetylide-ethylenediamine complex in DMSO.[24]

(E)-9, 11-Dodecadien-1-yl acetate(2)

A THF soln (35 ml) of 9 (27 g, 0.11 mol) was reacted at −10° to 0° with a THF soln of disiamylborane prepared starting from borane-methyl sulfide complex (0.128 mol) and 2-methyl-2-butene (0.256 mol) in THF (64 ml). The soln 10 was slowly added at 0° to a stirred yellow soln of tetrakis (triphenylphosphine)palladium (1.27 g) and vinylbromide (11.77 g, 0.11 mol) in THF (200 ml). Subsequently, a deaerated soln of NaOH (8.8 g, 0.22 mol) in water (110 ml) was added and the resulting mixture was heated under stirring to 50° for 4 hr. It was then cooled to room temp, AcOH (23 ml, 0.40 mol) was added and the mixture was heated under stirring for 12 hr. After cooling to room temp, 6.5 N NaOH (110 ml, 0.72 mol) was added, followed by addition of 36% H_2O_2 33 ml) maintaining the temp. below 40°. It was further stirred for 1 hr at 40°. The mixture was then cooled, filtered and worked up. Crude (E) - 1 - (2 - tetrahydropyranyloxy) - 9, 11 - dodecadiene was then reacted at 80° for 20 hr with AcOH (100 ml) and Ac_2O (55 ml). The mixture was poured into ice-water and extracted with ether. Fractional distillation of the dried and neutralized ether extracts gave (E)-2 in 54% yield: b.p. 80°/0.04 torr. Glc analysis (column at 155° for 14 min, then heated to 175° at 10°/min) showed that 2 (t_r = 8.7 min) had 87.7% chemical purity and contained several impurities (t_r = 2.3, 4.5, 4.9, 5.2, 5.4, 7.2, 9.7, 10.1, 10.9, 12.8, 13.1, 18.8 min). Thus a sample of 2 (9 g) was purified by column chromatography over SiO_2–$AgNO_3$ (prepared 200 g of Merck 70–230 mesh extra pure silica gel and 25.8 g of AgNO$_3$ in 200 ml of acetonitrile) in hexane.[33] Elution with hexane–ether (90:10) gave 2 (3 g) which contained less than 2.3% of impurities. Such compound had: b.p. 82°/0.04 torr; n_D^{25} 1.4642; $ν_{max}$ 3080, 3040, 3010, 2930, 2860, 1740, 1650, 1600, 1450, 1385, 1365, 1230, 1040, 1005, 950, 895, 725, 640, and 605 cm^{-1}. ^{1}H NMR (100 MHz, $CDCl_3$): δ 6.39–5.39 (3H, complex m), 5.09–4.76 (2H, m), 4.07 (2H, t), 2.01 (3H, s), 2.16–1.88 (2H, br), 1.80–1.20 ppm (12H, br). ^{13}C NMR: δ 20.93, 25.88, 28.61, 29.14, 29.32, 32.51, 64.51, 114.41, 130.79, 135.17, 137.15, 170.60 ppm. UV (heptane): $λ_{max}$ (ε) 225 nm (32,792). Mass spectrum: m/e 224(8.1%) M$^+$), 181(1.6%), 164(15.3%), 136(13.6%), 121(19.3%), 108(11.2%), 107(12.0%), 96(21.7%), 95(19.3%), 94(21.5%), 93(22.2%), 80(62.9%), 67(87.1%), 54(58%), 43(100%), 41(54.9%).

Elem. anal., found % (calcd. for $C_{14}H_{24}O_2$): C 75.13(74.95); H 10.60(10.78). Hplc analysis [UV detector = 232 nm; eluent = MeOH: water (3:1)(6 μl/min); substance load: 0.1 μl of soln of **2** (0.01 g) in MeOH (1 ml)] showed that **2** had stereoisomeric purity higher than 97%.

(E)-1-*Jodo*-1-*butene* (12)

1-Butyne (9.5 g, 0.176 mol) and catecholborane (21.2 g, 0.176 mol) were stirred in a 100 ml autoclave for 3 hr under N_2 at 70°. The mixture was cooled at room temp and stirred with water (176 ml) for 2 hr at 25°. The resulting mixture was cooled at 0° and the white solid formed was collected by filtration and washed free of catechol using ice-cold water. The boronic acid was then dissolved in ether (176 ml) and cooled to 0°. 3N NaOH (176 ml) was then added followed by an ether soln (528 ml) of I_2 (53.6 g, 0.211 mol), while stirring at 0°. The mixture was stirred for 3° min at 0°. The excess of I_2 was then destroyed with $Na_2S_2O_3$aq. The ether soln of (*E*) - 1 - iodo - 1 - butene was separated, washed with water, dried and concentrated at 350 torr. Glc analysis showed that **12** had stereoisomeric purity higher than 98.5% and was contaminated by traces of 1-butyne and ether. The yield (evaluated by glc) resulted to be ca 50%. Compound **12**, maintained at −25° in the dark, was used in the next step without any further purification.

(E)-11-*Tetradecen-9-yn-1-yl acetate* (14)

Compound **9** (16.78 g, 0.070 mol) dissolved in THF (60 ml) was added to a soln of EtMgBr (0.074 mol) in THF (50 ml). After the addition was complete, heating was continued for 1 hr. The THF soln of **13** was then slowly added to a mixture of tetrakis(triphenylphosphine)palladium (4.07 g, 3.52 mmol) and (*E*) - 1 - iodo - 1 - butene (0.70 mol) in benzene (120 ml) and stirred for 3.5 hr at 20° and for 0.5 hr at 60°. It was then cooled at room temp and hydrolyzed with ice-cold water. The organic layer was separated and the aqueous layer was extracted with five portions (50 ml) of hexane. The combined extracts were washed twice with sat NaCl aq, passed over a short alumina column, and concentrated *in vacuo*. The residue (19.6 g) was acylated with Ac_2O and AcOH, yielding **14** in 68% overall yield; b.p. 108/0.03 torr; n_D^{25} 1.4725; ν_{max} 3020, 2970, 2940, 2860, 2220, 1740, 1450, 1430, 1385, 1365, 1240, 1030, 955, and 720 cm^{-1}; ^{1}H NMR (60 MHz, CDCl$_3$): δ 6.0–4.9 (m, 2H), 3.77 (t, 2H), 2.4–1.8 (br, 4H), 1.90 (3H, s), 1.8–1.2 (br, 12H), and 0.93 ppm (3H, t). ^{13}C NMR: δ 13.10, 19.34, 20.96, 25.93, 28.21, 28.67, 28.79, 29.03, 29.13, 64.51, 79.19, 88.52, 108.99, 144.36 ppm. Mass spectrum: m/e 250 (M$^+$) (0.9%), 161(2%), 94(100%), 61(2.7%), 43(35%). Found: C, 76.85; H, 10.53. Calc. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47%. Glc analysis (column at 185°, tr = 10.6 min) showed that **14** had chemical and stereoisomeric purity higher than 99%.

(9Z, 11E)-9, 11-*Tetradecadine-1-yl acetate* (3)

Compound **14** (8.01 g, 0.032 mol) was converted in 89% yield into **3**, by hydroboration with disiamylborane, followed by protonolysis with AcOH and oxidation with 36% H_2O_2 in alkaline soln, Compound **3** had: b.p. 107–108°/0.05 torr; n_D^{25} 1.4707; ν_{max} 3020, 2960, 2930, 2855, 1730, 1460, 1385, 1365, 1240, 1040, 980, 840, 780, 720, 630, and 605 cm^{-1}. ^{1}H NMR (100 MHz, CDCl$_3$): δ 6.6–5.2 (m, 4H), 4.16 (t, 2H), 2.5–2.0 (m, 4H), 2.14 (s, 3H), 1.9–1.2 (br, 12H), 1.09 ppm (t, 3H). ^{13}C NMR: δ 13.66, 20.94, 25.89, 27.64, 28.63, 28.86, 29.21, 29.38, 29.68, 30.08, 64.53, 124.56, 128.52, 129.80, 135.88, 170.78 ppm. Mass spectrum: m/e 252 (M$^+$)(8%), 192 (M$^+$–CH$_3$COOH) (5%), 163(2.5%), 149(5%), 135(10%), 121(17%), 95(54%), 82(64%), 79(59%), 67(100%), 61(5%), 43(92%). UV (heptane): λ_{max} (ϵ): 233 nm (30.246). Elem. anal., found % (calcd. for $C_{16}H_{28}O_2$): C 75.86 (76.03); H 11.34 (11.18). Glc analysis (column at 175°; tr = 8.5 min) showed that **3** had 99% chemical purity and 98.7% stereoisomeric purity.

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