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NEW STEREOSPECIFIC SYNTHESES OF PHEROMONE BOMBYKOL AND ITS THREE GEOMETRICAL ISOMERS[1]

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Abstract—New stereospecific syntheses of the pheromone bombykol and its three geometrical isomers are achieved by palladium-catalyzed cross-coupling reaction between an appropriate alkenylborane and an alkenyl halide in the presence of a base.

Bombykol is a well-known pheromone, first isolated from *Bombyx mori* L by Butenandt *et al.* Later, the structure was clarified by the same investigators.[3] The first syntheses of bombykol and the three geometrical isomers by employing the Wittig reaction were achieved by Butenandt and his colleagues[4] as well as by Truscheit and Eiter.[5] Since then, the synthesis of bombykol has been reported by three groups of investigators.[6–8]

In this paper we wish to report the achievement of new stereospecific syntheses of bombykol and its three geometrical isomers by use of the palladium-catalyzed cross-coupling reaction between an alkenylborane and an appropriate haloalkene in the presence of a base. We described the method itself in our previous paper,[9] and we believe that the present results show that the method developed by us is a powerful and reliable one for stereospecific syntheses of conjugated dienes using alkenylboranes.

The alkenylboranes and the alkenylboronic acids required for the present couplings were 11-hydroxyundecenylboronic acid **4**, (Z)-1-pentenyldisiamylborane **6**, and (*E*)-1-pentenyl-1,3,2-benzodioxaborole **8**. These were newly prepared by hydroboration of appropriate acetylenic precursors (Scheme 1).

Thus, bromination of 10-undecen-1-ol **1** at − 10–0° gave 10,11-dibromoundecan-1-ol in a nearly quantitative yield.

Dehydrobromination of this dibromoundecan-1-ol with sodium amide in liquid ammonia[10] afforded 10-undecyn-1-ol **2** as a viscous oil in a 60% yield. This acetylenic alcohol **2**, without protecting the hydroxy group, was subjected to hydroboration with 1,3,2-benzodioxaborole[11] to afford a borole (**3**); it was then immediately hydrolyzed at room temperature to give (*E*)-11-hydroxy-1-undecenylboronic acid **4**, an amorphous solid. The yield of **4** from **2** was 83%.

(Z)-1-Pentenyldisiamylborane **6** was then prepared by hydroboration of 1-bromo-1-pentyne **5**[12] with disiamylborane in a 90% yield according to the literature procedure.[13] The assigned geometry was confirmed by the ^{1}H NMR spectrum which showed the two olefinic protons at δ 5.8 ~ 6.2 as a multiplet. The absence of any signals due to olefinic protons having (*E*) configuration, which should appear at δ 6.25 (d, 1H) and δ 6.5 ~ 7.15 (dt, 1H),[14] proved that the isomeric purity of borane **6** exceeded 99%.

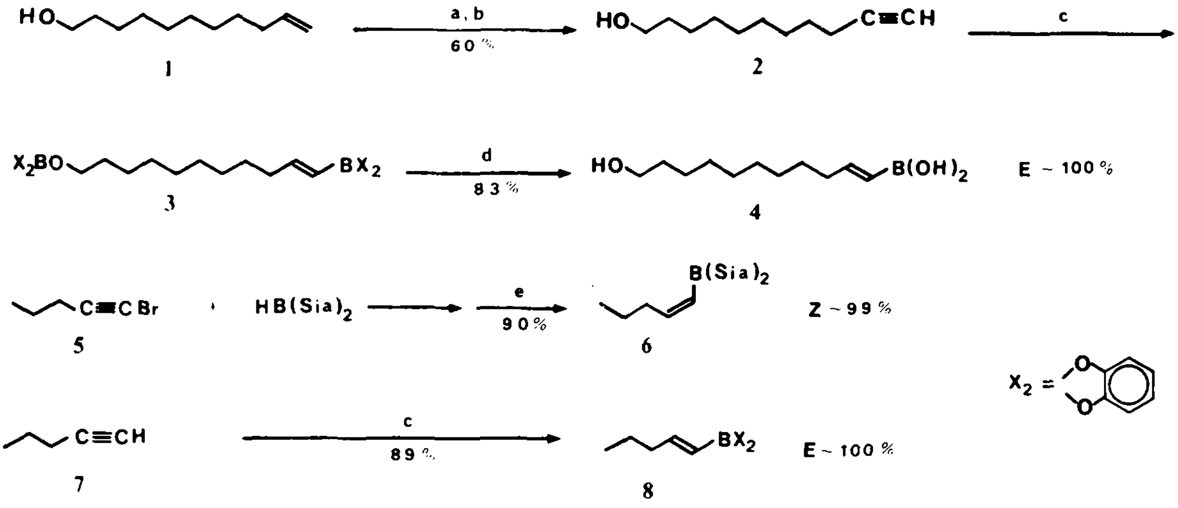
Finally, (*E*)-pentenyl-1,3,2-benzodioxaborole **8** was prepared by hydroboration[11] of 1-pentyne **7** with 1,3,2-benzodioxaborole in an 89% isolated yield. The borole **8** was a liquid which was stable in air. The geometry of the olefinic protons was again confirmed by the ^{1}H NMR spectrum.

On the other hand, the four haloalkenes, (*Z*)-1-bromo-1-pentene **9**, (*E*)-1-iodo-1-pentene **11**, (*E*)-11-iodo-10-undecen-1-ol **12** and (*Z*)-11-bromo-10-undecen-1-ol **13**, were prepared by stereospecific halogenolysis[15–17] of boronic acid **4** and borole **8** according to the procedure reported by Brown *et al.* (Scheme 2).

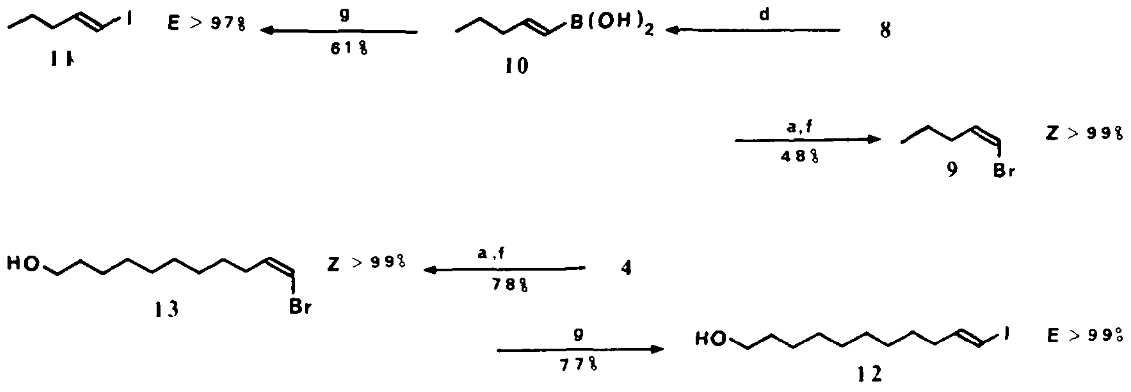
Thus, the treatment of (*E*)-1-pentenyl-1,3,2-benzodioxaborole **8** with bromine followed by one with sodium methoxide in methanol resulted in the replacement of borane by bromine with an inversion of the configuration[15] and gave (*Z*)-1-bromo-1-pentene **9** in a 48% yield. The olefinic protons in the ^{1}H NMR spectrum was identical with that of (*Z*)-11-bromo-10-undecen-1-ol **13**. Analysis by GLC indicated that the (*Z*)-isomer in bromide **9** exceeded 99%.

Hydrolysis of borole **8** with water to give an amorphous (*E*)-1-pentenylboronic acid **10** and its treatment with sodium hydroxide followed by iodine according to the procedure by Brown *et al.*[17] resulted in the replacement of boronic acid by iodine with the retention of the configuration to give (*E*)-1-iodo-1-pentene **11** in a 61% yield. The geometry of the olefinic protons as assigned was confirmed by the ^{1}H NMR spectrum which showed a doublet at δ 6.07 with $J = 15$ and 6.5 Hz. Analysis of the iodide **11** by GLC indicated that the ratio of (*Z*)- and (*E*)-isomer in the product was 3:97.

Analogously, using the procedure described above, (*E*)-11-iodo-10-undecen-1-ol **12** and (*Z*)-11-bromo-10-undecen-1-ol **13**., were readily prepared by stereospecific halogenolysis of boronic acid **4** with iodine and with bromine in 77% and 78% yields respectively.



Scheme 1.



Scheme 2.

Analysis by GLC indicated that the isomeric purity of halides **12** and **13** exceeded 99%.

Cross-coupling reactions

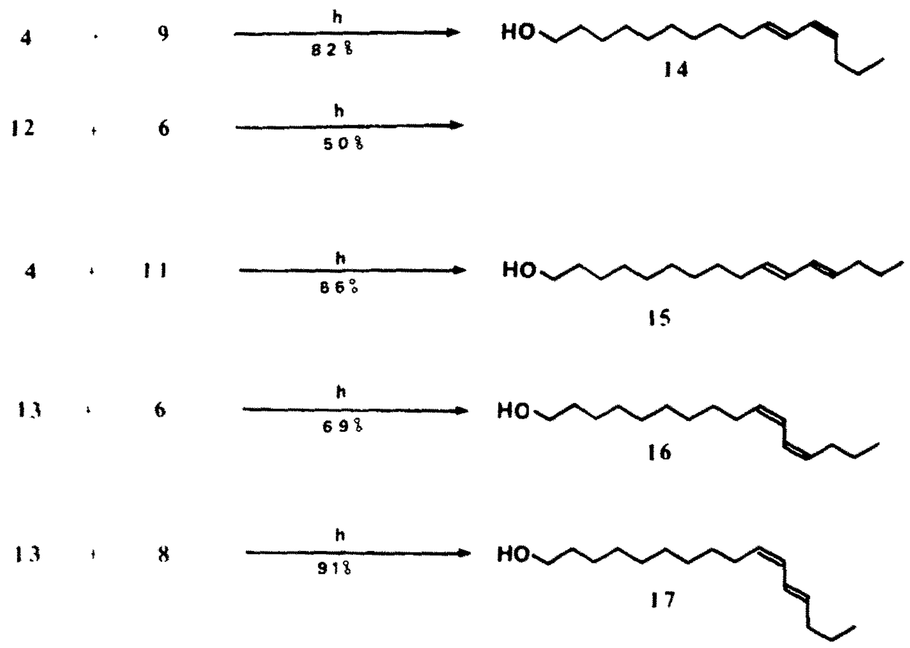
A mixture of 11-hydroxy-1-undecenyl boronic acid **4** and (*Z*)-1-bromo-1-pentene **9** in benzene containing $Pd(PPh_3)_4$[18] and sodium ethoxide was heated under reflux for 2.5 hr in a nitrogen atmosphere. An excess of boronic acid was then removed by oxidation with a 30% hydrogen peroxide and sodium hydroxide. A normal work-up and distillation of the product by means of a Kugelrohr gave bombykol **14** (Scheme 3). Analysis of the crude product by GLC indicated that the yield of bombykol was an 82%. A ^1H NMR spectrum (400 MHz, Fig. 1) of the synthetic bombykol showed that a pattern of the coupling of the olefinic protons was identical with that of the (5*E*, 7*Z*)-5,7-tetradecadiene prepared by us[9] and the isomeric purity was 96%, containing a 4% of (10*E*, 12*E*)-isomer which could not be removed by preparative GLC. The chemical shifts and the coupling constants are shown in Table 1.

An alternative synthesis of bombykol was carried out by cross-coupling between eleven-carbon haloalkene and five-carbon alkenyl borane; 11-iodo-10-undecen-1-ol **12** reacted with (*Z*)-1-pentenyldisiamyl borane in benzene containing $Pd(PPh_3)_4$ and sodium ethoxide to give bombykol in a 50% yield GLC (Scheme 3).

The syntheses of three geometrical isomers of bombykol were then undertaken (Scheme 4).

Thus, cross-coupling of boronic acid **4** with (*E*)-1-iodo-1-pentene **11** under conditions similar to the synthesis of bombykol and the distillation of the product by using a Kugelrohr gave (10*E*, 12*E*)-hexadecadien-1-ol **15** in a 53% isolated yield (a 66% yield by GLC). A ^1H NMR spectrum (400 MHz, Fig. 2) indicated that the synthetic (10*E*, 12*E*)-isomer was virtually free from other isomers. The pattern of the coupling of the olefinic protons in a ^1H NMR spectrum of the synthetic dienol **15** was nearly identical with that of the (7*E*, 9*E*)-hexadecadiene which we had previously prepared.[9]

Syntheses of the remaining two geometrical isomers of bombykol were accomplished by the stereospecific coupling reactions of an eleven-carbon haloalkene and a five-carbon alkenyl borane; 11-bromo-10-undecen-1-ol **13** and (*Z*)-1-pentenyl disiamyl borane **6** in benzene were subjected to cross-coupling in the presence of $Pd(PPh_3)_4$ and sodium ethoxide to yield (10*Z*, 12*Z*)-hexadecadien-1-



a, Br_2 b, $NaNH_2$ NH_3 c, HBX_2 d, H_2O e, t-BuLi f, NaOMe g, NaOH / I_2

h, PdL_4 / NaOEt / benzene

Scheme 3

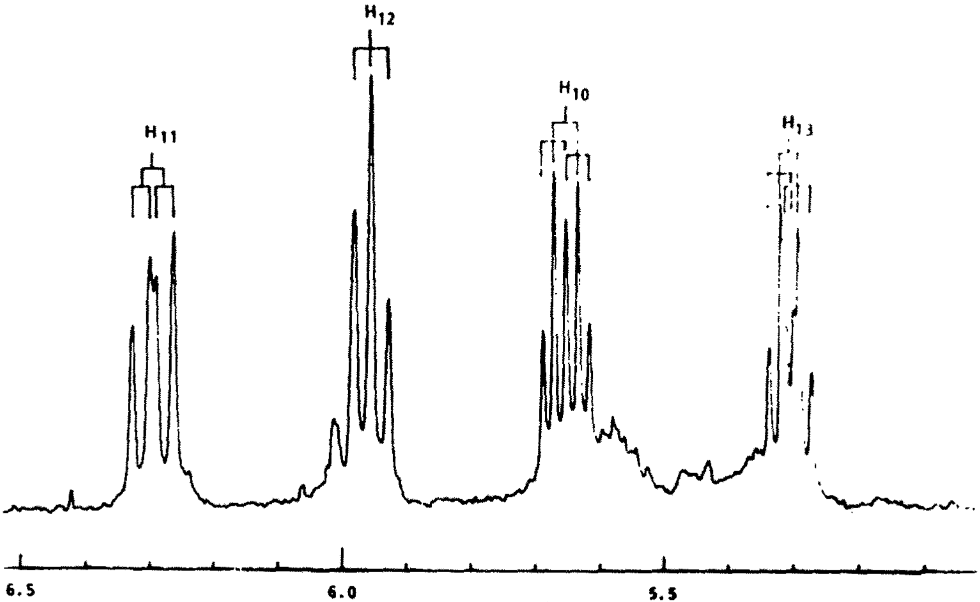


Fig. 1. The olefinic proton signals in 400 MHz ^1H NMR spectrum of bombykol.

ol **16** in a 59% isolated yield (69% yield by GLC). Similarly, cross-coupling of bromoalkene **13** with (*E*)-1-pentenyl-1,3-benzodioxaborole **8** gave (10*Z*, 12*E*)-hexadecadien-1-ol **17** in a 77% isolated yield (a 91% yield by GLC). Signals due to the olefinic protons in 400 MHz ^1H NMR spectra of synthetic dienols **16** and **17** are shown in Figs. 3 and 4. The spectra indicated that the synthetic (10*Z*, 12*Z*)- and (10*Z*, 12*E*)-isomers **16** and **17** were virtually free from other isomers. The patterns of the couplings of the dienols **16** and **17** were nearly identical with those of (5*Z*, 7*Z*)-5,7-tetradecadiene[9] and bombykol respectively, thus confirming the geometry of their diene moieties. The ^1H NMR data of the olefinic protons of the three synthetic geometrical isomers of bombykol are shown in Table 1.

EXPERIMENTAL

IR spectra were recorded with a Hitachi-Perkin-Elmer Model 125 spectrometer. ^1H NMR spectra ($CDCl_3$ solution) of all the compounds with the exceptions of synthetic bombykol and its

Table 1. Chemical shifts (δ) and coupling constants (Hz) of the olefinic protons of bombykol and the three geometrical isomers ($CDCl_3$-TMS, 400 MHz)

compd.	10-H	11-H	12-H	13-H
14 (10E, 12Z, bombykol)	5.65 dt(15 and 6.8) $J_{9\text{-}H,10\text{-}H}=6.8$ $J_{10\text{-}H,11\text{-}H}=15$	6.30 dd(15 and 11) $J_{11\text{-}H,12\text{-}H}=11$	5.96 dd(11 and 11) $J_{12\text{-}H,13\text{-}H}=11$	5.30 dt(11 and 7.3) $J_{13\text{-}H,14\text{-}H}=7.3$
15 (10E, 12E)	5.56 or 5.57 dt(6.8 and 14.2 or 6.8 and 11.7) $J_{9\text{-}H,10\text{-}H}=6.8$ $J_{10H,11\text{-}H}=11.7$ or 14.2	5.98 or 6.01 dd(6.8 and 11.7 or 6.8 and 14.2) $J_{11\text{-}H,12\text{-}H}=6.8$	5.98 or 6.01 dd(6.8 and 11.7 or 6.8 and 14.2) $J_{12\text{-}H,13\text{-}H}=11.7$ or 14.2	5.56 or 5.57 dt(6.8 and 14.2 or 6.8 and 11.7 $J_{13\text{-}H,14\text{-}H}=6.8$
16 (10Z, 12Z)	5.42 dt(9.3 and 7.6) $J_{9\text{-}H,10\text{-}H}=7.6$ $J_{10\text{-}H,11\text{-}H}=9.3$	6.26 d(9.3)	6.26 d(9.3)	5.42 dt(9.3 and 7.6) $J_{12\text{-}H,13\text{-}H}=9.3$ $J_{13\text{-}H,14\text{-}H}=7.6$
17 (10Z, 12E)	5.30 dt(11 and 7.5) $J_{9\text{-}H,10\text{-}H}=7.5$ $J_{10\text{-}H,11\text{-}H}=11$	5.95 dd(11 and 11) $J_{11\text{-}H,12\text{-}H}=11$	6.30 dd(11 and 15) $J_{12\text{-}H,13\text{-}H}=15$	5.66 dt(7.3 and 15) $J_{13\text{-}H,14\text{-}H}=7.3$

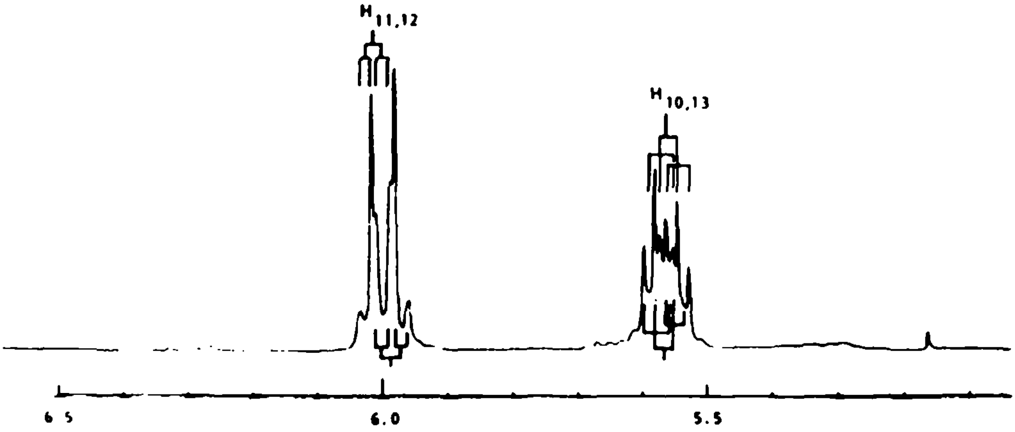


Fig. 2. The olefinic proton signals in 400 MHz ^1H NMR spectrum of (10*E*, 12*E*)-hexadecadien-1-ol **15**

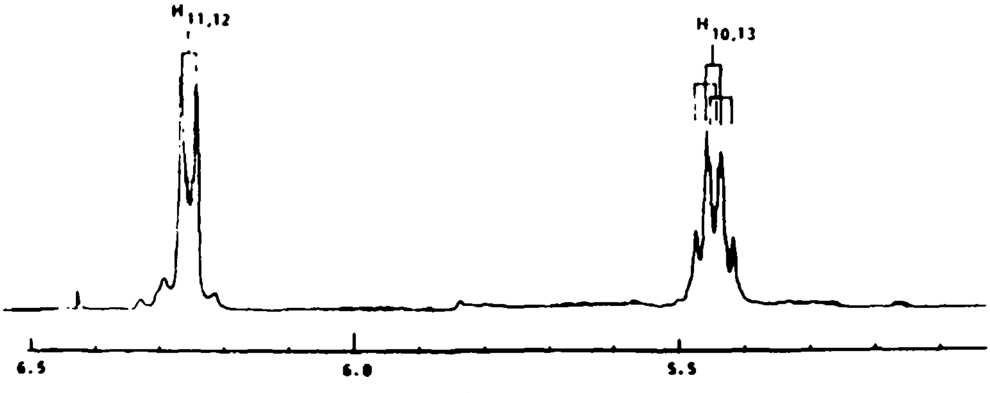


Fig. 3. The olefinic proton signals in 400 MHz ^1H NMR spectrum of (10*Z*, 12*Z*)-hexadecadien-1-ol **16**

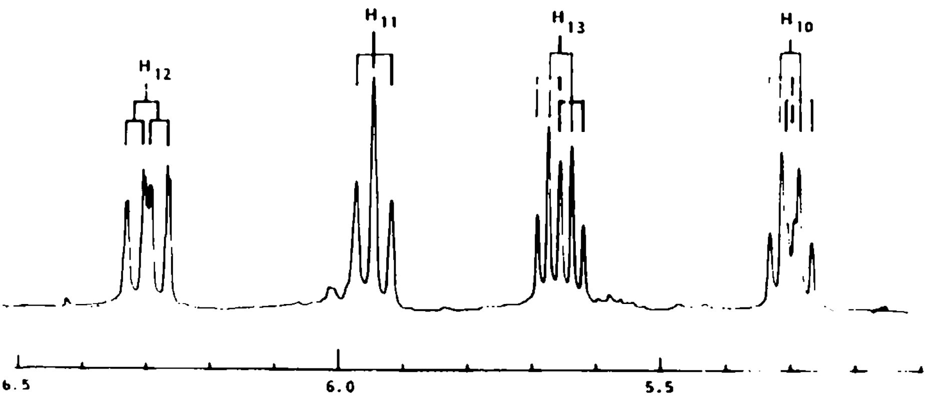


Fig. 4. The olefinic proton signals in 400 MHz ^{1}H NMR spectrum (10*Z*, 12*E*)-hexadecadien-1-ol **17**.

three geometrical isomers were determined with a Hitachi R-22 spectrometer (90 MHz). ^{1}H NMR spectra of the synthetic bombykol and its three isomers were recorded with JEOL JNM FX-400 spectrometer (400 MHz). Chemical shifts are reported in δ units downfield from TMS as an internal standard.

10-*Undecen*-1-*ol* **1**

To lithium aluminum hydride (8 g) in dry diethyl ether (300 ml; distilled from benzophenone ketyl) placed in a 1-l. three-necked flask fitted with a mechanical stirrer, a dropping funnel and a condenser (protected from moisture by calcium chloride tube), was added dropwise methyl 11-undecenoate (65 g) in dry diethyl ether (100 ml) in the course of 2 hr , while the solution was under reflux. The solution was then heated under reflux for another 1 hr. To the ice-cooled solution dilute sulphuric acid (200 ml) was cautiously added to decompose an excess of hydride. The solution was then extracted with diethyl ether (50 ml × 3). The combined organic layer was washed with a 5% sodium carbonate solution, a brine and water, and dried over anhydrous magnesium sulphate. The product was purified by distillation to give 53 g (95%) of 10-undecen-1-ol **1**, b.p. 133° (14 mm) lit.[8] 123–125°/6 mm).

11-*Undecyn*-1-*ol* **2**

To a solution of 10-undecen-1-ol **1** (53 g, 0.312 mol) in dry diethyl ether (150 ml) was added dropwise bromine (50 g, 0.312 mol) at − 10–0° over a period of 30 min. Diethyl ether was then removed under reduced pressure (15 mm) to give 10,11-dibromoundecan-1-ol (103 g, 100%). To the solution prepared from sodium (10.12 g) and liquid ammonia (300 ml) was added dropwise a solution of 10,11-dibromoundecan-1-ol (33 g, 0.1 mol) in diethyl ether (20 ml) in the course of 20 min while the liquid ammonia solution was under reflux. The solution was left under reflux for another 30 min and ammonia was removed, leaving a solid residue. To this residue were added crushed ice (200 g) and then cold water (200 ml) to dissolve the solid. The solution was extracted with diethyl ether, washed with a dilute hydrochloric acid, brine and water, and then dried over anhydrous potassium carbonate. Distillation of the residue gave 11-undecyn-1-ol **2** (10.1 g, 60%) as a viscous oil, b.p. 138° (16 mm). IR (neat), 3320 (broad OH), 3320 ($HC\equiv C$–), 2128 ($C\equiv C$–), 1465, 1062, and 632 cm^{-1}; ^{1}H NMR, 1.2–1.7 (14 H, m, –CH_2–), 1.89 (1H, t, J = 3 Hz, $HC\equiv C$–), 2.05–2.30 (2H, m, –$CH_2C\equiv C$–), and 3.62 (2H, t, J = 6 Hz, –CH_2O–).

Preparation of (E)-11-*hydroxy*-1-*undecenylboronic acid* **4**

To 10-undecyn-1-ol (1.51 g, 9 mmol) in dry THF (3 ml) was added dropwise 1,3,2-benzodioxaborole[11] (2.0 ml, 18 mmol) at room temperature. After the evolving of hydrogen had ceased, the mixture was heated under reflux for 5 hr. To the cooled reaction mixture was added water (60 ml). The mixture was stirred for 2 hr at 20° to hydrolize the ester **3**. Boronic acid **4** was collected by filtration after the reaction mixture had cooled to 0°. The boronic acid[4] was washed with water (20 ml × 3) to remove the last traces of catechol. The yield was 1.6 g (83%). It may be recrystallized with a large volume of water to yield colourless crystals, m.p. 55–56°. For the coupling reaction, boronic acid was used without a further recrystallization.

(Z)-1-*Pentenyldisiamylborane* **6**

This borane was prepared from 1-bromo-1-pentyne **5**[12] according to the reported procedure.[13] The borane (6 g; 90%) was obtained from 4.41 g of 1-bromo-1-pentyne. No olefinic proton signals due to (*E*)-isomer were found in the ^{1}H NMR spectrum, proving the absence (< 1%) of the (*E*)-isomer.

Preparation of (E)-1-*pentenyl*-1,3,2-*benzodioxaborole* **8**

In a dry 25-ml flask were placed 1-pentyne (7.9 ml, 80 mmol) and 1,3,2-benzodioxaborole[11] (8.5 ml, 76.5 mmol) with the aid of a hypodermic syringe. The mixture was heated under reflux for 5 hr while it was stirred with the temperature of the bath at 70°. Distillation of the product under reduced pressure gave a borane **8**, b.p. 69° 0.3 mm, (12.8 g, 89%). This borane was a transparent liquid and was stable in air. It was gradually hydrolyzed to form white precipitates of boric acid when exposed to moisture. IR. (neat) 1637, 1468, 1399, 1369, 1329, 1233, 805, and 738 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.96 (3H, t, J = 7 Hz, $\underline{CH_3}CH_2$–), 1.55 (2H, q–t, J = 7 and 7 Hz, $CH_3\underline{CH_2}CH_2$–), 2.29 (2H, d–t, J = 6 and 7 Hz, $CH_3CH_2\underline{CH_2}CH$=), 5.86 (1H, broad d, J = 18 Hz, –CH=$\underline{CH}$–B).

(Z)-1-*bromo*-1-*pentene* **9**

To (*E*)-1-pentenyl-1,3,2-benzodioxaborole **8** (3.76 g, 20 mmol) in dry dichloromethane (30 ml) cooled to 0° was added dropwise bromine (6.4 g, 40 mmol) in dry carbon tetrachloride (10 ml) in the course of 20 min and the solution was stirred for 1 hr. To this solution was added dropwise 2M sodium ethoxide in ethanol (40 ml) at 0° and the solution was stirred for 30 min. After the addition of water (20 ml) to the solution, the organic layer was extracted with dichloromethane (20 ml × 2). The solution was washed with water and dried over anhydrous magnesium sulphate. The usual work-up afforded a product which was distilled under reduced pressure to give (*Z*)-1-bromo-1-pentene, b.p. 41° (92 mm) (1.4 g, 48%). Analysis of the bromide by GLC (Hitachi K-53, SVS capillary column, 0.25 mm × 45 m, squalene) indicated that (*Z*)-isomer in the bromide exceeded 99%. ^{1}H NMR ($CDCl_3$) 0.92 (3H, t, J = 7 Hz, CH_3CH_2–), 1.48 (2H, t–q, J = 7 and 7 Hz, $CH_3\underline{CH_2}$–), 2.21 (2H, d-t, J = 6 and 7 Hz, $CH_3CH_2\underline{CH_2}$–CH=), and 6.1 ~ 6.3 (2H, m, –CH=CH–).

Preparation of (E)-1-*iodo*-1-*pentene* **11**

To water (25 ml) was a added (*E*)-1-pentenyl-1,3,2-benzodioxaborole **8** (4 g, 21 mmol) and the reaction mixture was stirred for 2 hr at room temperature while the mixture was exposed to air. After the mixture was cooled to 0° (*E*)-1-pentenylboronic acid **10** was collected by filtration and washed with cold water to remove catechol. The boronic acid (2.3 g, 94%) obtained was a colourless solid. To a solution of boronic acid **10** (2.2 g, 19.3 mmol) in diethyl ether (20 ml) at 0°, was added 3M sodium hydroxide in water (20 ml) and then iodine (6 g) in diethyl ether (60 ml) over a period of 30 min. The solution was stirred for

30 min and the excess of iodine was decomposed by adding a few drops of a saturated sodium thiosulphate. The organic layer was dried over magnesium sulphate. The normal work-up gave a product which was distilled under reduced pressure to afford (*E*)-1-iodo-1-pentene **11**, b.p. 53° (25 mm). Analysis of the iodide by GLC indicated th ratio of (*Z*)- and (*E*)-isomer to be 3:97. IR, (neat), 1606, 1460, 1235, 1189, 945, and 662 cm^{-1}; 0.92 (3H, t, J = 7 Hz, $\underline{CH_3}CH_2$–), 1.44 (2H, t–q, J = 7 and 7 Hz, $CH_3\underline{CH_2}$–), 2.07 (2H, d–t, J = 6 and 7 Hz, $CH_3CH_2\underline{CH_2}$–CH=), 6.06 (1H, d, J = 15 Hz, CH=$\underline{CH}$I), and 6.61 (1H, d-t, J = 7 and 15 Hz, $\underline{CH}$=CHI).

(E)-11-*Iodo*-10-*undecen*-1-*ol* **12**

(*E*)-11-Hydroxy-1-undecenylboronic acid **4** (1.5 g, 7 mmol) in diethyl ether (20 ml) containing 1.5M sodium hydroxide in water (30 ml) was placed in a 100-ml flask and the solution was stirred for 30 min. Part of the boronic acid remained undissolved in the solution. To the solution was added dropwise iodine (2 g) in diethyl ether (20 ml) over a period of 30 min and the solution was stirred for a further 30 min at 0°. Excess of iodine was decomposed by adding a few drops of a saturated sodium thiosulphate solution. The organic layer was dried over anhydrous magnesium sulphate. The normal work-up gave a product which was distilled by use of a Kugelrohr to afford (*E*)-11-iodo-10-undecen-1-ol **12**, b.p. 100–110° (0.1 mm) (oven temp. of the Kugelrohr), m.p. 23.5° (Melt-Temp). GLC analysis showed >99% of (*E*)-iodide (15% SE-30 on Uniport B, 2 m). IR (neat), 3400 (OH), 1605, 1466, 1187, 1058,936, and 662 cm^{-1}; ^{1}H NMR, (CDCl$_3$), 1.30 (14 H, broad s, OH–CH$_2$$\underline{(CH_2)_7}$–CH$_2$–), 1.9 ~ 2.2 (2H, m, –$\underline{CH_2}$–CH=), 3.68 (2H, t, J = 6 Hz, HO–$\underline{CH_2}$–), 6.02 (1H, d, J = 15 Hz, CH=$\underline{CHI}$), and 6.58 (1H, d-t, J = 15 and 7 Hz).

Preparation of (Z)-11-*bromo*-10-*undecen*-1-*ol* **13**

To 11-hydroxy-1-undecenylboronic acid **4** (2.45 g, 11.4 mmol) in chloroform (30 ml) cooled at −10°C was added dropwise bromine (1.92 g) in carbon tetrachloride (4 ml) for 15 min and the solution was stirred for 1 hr at −10–0°. A few drops of a saturated sodium thiosulphate solution were added to decompose an excess of bromine and then 2M sodium ethoxide in ethanol (12 ml) was added over a period of 16 min at 0°. The solution was stirred for 30 min and water (20 ml) was added. The aqueous layer was extracted with chloroform (20 ml × 2). The combined organic layer was washed with water and dried over anhydrous magnesium sulphate. The usual work-up gave a product which was distilled by use of a Kugelrohr to give (*Z*)-11-bromo-10-undecen-1-ol **13**, b.p. 90–95° (0.1 mm, oven temp). GLC (10% silicone OV-17 on Uniport B, 2 m) indicated >99% (*Z*)-isomer (a single peak in GLC). IR, (neat), 3350 (broad, OH), 1620, 1060, 700, and 670 cm^{-1}; ^{1}H NMR, (CDCl$_3$), 1.33 (14 H, broad s, HO–CH$_2$$\underline{CH_2}$)$_7CH_2$–), 2.1 ~ 2.4 (2H, m, –$\underline{CH_2}$–CH=), 3.68 (2H, t, J = 6 Hz, HO–$\underline{CH_2}$–), and 6.0 ~ 6.4 (2H, m, –$\underline{CH}$=$\underline{CH}$Br).

Synthesis of Bombykol **14**

(a) A dry 50 ml flask equipped with a septum inlet, a magnetic stirring bar, a reflux condenser was flushed with nitrogen. In the flask was replaced Pd(PPh$_3$)$_4$ (0.29 g, 0.25 mmol) in benzene (20 ml), (*Z*)-1-bromo-1-pentene (9-G) (0.754 g, 5 mmol), 11-hydroxy-1-undecenylboronic acid **4** and 2M sodium ethoxide in ethanol (5 ml) under N$_2$. The solution was heated under reflux for 2.5 hr while stirring. The reaction mixture was cooled to room temperature and the removal of the excess borane by oxidation was accomplished by the addition of aqueous sodium hydroxide (3M solution, 0.5 ml) and a 30% hydrogen peroxide solution (0.5 ml) over a period of 1 hr. The crude bombykol was extracted with diethyl ether, washed with a saturated sodium chloride solution, and dried over anhydrous magnesium sulphate. An analysis of the product by GLC (Hitachi 163, 10% silicone OV-17 on uniport,B, 2 m. Lauryl alcholol as an internal standard) indicated that the product contained 4.1 mmol (82%) of (10*E*, 12*Z*)-hexadecadien-1-ol **14** (bombykol). Distillation of this product by Kugelrohr gave bombykol, b.p. 125°/0.1 mm (oven temp. of the Kugelrohr) (lit.[7] 119–120°/0.001 nm). n_D^{20}1.4835 (lit.[5] n_D^{20} = 1.4835); IR, (neat), 3320 (broad, OH), 980 and 945 cm^{-1}; ^{1}H NMR (CDCl$_3$), (400 MHz, Fig. 1), 0.92 (3H, t, J = 7.6 Hz, $\underline{CH_3}CH_2$–), 1.2 ~ 1.7 (16H, m, HOCH$_2$$\underline{(CH_2)_7}$– and $\underline{CH_2}$CH$_3$), 1.9 ~ 2.2 (4H, m, –$\underline{CH_2}$CH=), 3.63 (2H, t, J = 6.9 Hz, HO–$\underline{CH_2}$–).

(b) Pd(PPh$_3$)$_4$ (0.29 g, 0.25 mmol) in benzene(20 ml), 11-iodo-10-undecen-1-ol **12**, (1.48 g, 5 mmol), (*Z*)-1-pentenyldisiamylborane **6**, (7.5 ml of 1M benzene solution, 7.5 mmol) and 2M sodium ethoxide in ethanol (5 ml) were heated under reflux for 2.5 hr. After the usual work-up, a benzene extract analyzed by GLC indicated that the yield of bombykol was 50%.

Synthesis of (10E, 12E)-*hexadecadien*-1-*ol* **15**

A mixture of Pd(PPh$_3$)$_4$ (0.29 g, 0.25 mmol) in benzene (20 ml), (*E*)-1-iodo-1-pentene **11**, (1.08 g, 5.5 mmol), (*E*)-11-hydroxy-1-undecenyl boronic acid **4** (1.07 g, 5 mmol), and 2M sodium ethoxide in ethanol (5 ml) were heated under reflux for 2.5 hr. The reaction mixture was worked up as usual to give a crude product. GLC showed that the yield of (10*E*, 12*E*)-hexadecadien-1-ol **15** was 66% (3.3 mmol). ^{1}H NMR (Fig. 2) showed that the isomers were virtually absent. Distillation gave a 0.63 g (59%) pure product, b.p. 100–110° 0.04 mm Hg (oven temp of Kugelrohr) m.p. 34° (lit.[5] m.p. 39–40°); IR, (neat), 3350 (OH), 1621, 1463, 1058, 984, 738 and 718 cm^{-1}; ^{1}H NMR (CDCl$_3$), 0.90 (3H, t, J = 7.3 Hz, $\underline{CH_3}CH_2$), 1.28 ~ 1.70 (16H, m, HOCH$_2$$\underline{(CH_2)_7}$– and –$\underline{CH_2}CH_3$), 2.0 ~ 2.07 (4H, m, –$\underline{CH_2}$–CH=), 3.63 (2H, t, J = 6.8 Hz, HO–$\underline{CH_2}$–).

Synthesis of (10Z, 12Z)-*hexadecadien*-1-*ol* **16**

A mixture of Pd(PPh$_3$)$_4$ (0.29 g, 0.25 mmol) in benzene (20 ml), (*Z*)-11-bromo-10-undecen-1-ol **13** (1.33 g, 5.3 mmol), (*Z*)-1-pentenyldisiamyl borane **6** (7.5 ml of 1M benzene solution, 7.5 mmol) and 2M sodium ethoxide in ethanol (5 ml) was heated under reflux for 2.5 hr. The reaction mixture was worked up as usual to give a product which was analyzed by GLC. This analysis indicated that the yield of the diene was 69% (3.45 mmol). ^{1}H NMR (Fig. 3) showed that the isomers were virtually absent. Distillation of the product gave 0.70 g (59%) of pure diene **16**, b.p. 120–130° 0.1 mm Hg (oven temp of Kugelrohr) (lit.[5] m.p. 25–26°). IR (neat), 3330 (broad OH), 1600, 1463, 1061, and 721 cm^{-1}; ^{1}H NMR (CDCl$_3$), 0.92 (3H, t, J = 7.6 Hz, CH$_3$CH$_2$), 1.29 ~ 1.70 (16H, m, HOCH$_2$$\underline{(CH_2)_7}$– and –$\underline{CH_2}CH_3$), 2.13 ~ 2.17 (4H, m, –$\underline{CH_2}$–CH=), 3.64 (2H, t, J = 6.6, HO–$\underline{CH_2}$–).

Synthesis of (10Z, 12E)-*hexadecadien*-1-*ol* **17**

A mixture of Pd(PPh$_3$)$_4$ (0.29 g, 0.25 mmol) in benzene (20 ml), (*Z*)-11-bromo-10-undecen-1-ol **13** (1.33 g, 5.3 mmol), (*E*)-1-pentenyl-1,3,2-benzodioxaborole **8** (1.05 g, 5.6 mmol) and 2M sodium ethoxide in ethanol (5 ml) was heated under reflux for 2.5 hr. The reaction mixture was worked up as usual and the product was analyzed by GLC. This indicated that the yield of the diene was 91% (4.44 mmol). ^{1}H NMR (Fig. 4) showed the absence of other isomers. Distillation of the crude product gave 0.92 g of a pure diene (77%), b.p. 100° 0.05 mm Hg (oven temp of Kugelrohr). n_D^{20} = 1.4821 [lit.[5] n_D^{20} = 1.4840]; IR, (neat), 3330, (broad, OH), 1465, 1055, 980, and 945 cm^{-1}; ^{1}H NMR (CDCl$_3$), 0.91 (3H, t, J = 7.3 Hz, $\underline{CH_3}CH_2$), 1.29 ~ 1.70 (16H, m, HOCH$_2$(CH$_2$)$_7$– and –$\underline{CH_2}$CH$_3$), 2.05 ~ 2.16 (4H, m, –$\underline{CH_2}$–CH=), 3.64 (2H, t, J = 6.6, HO–$\underline{CH_2}$–).

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