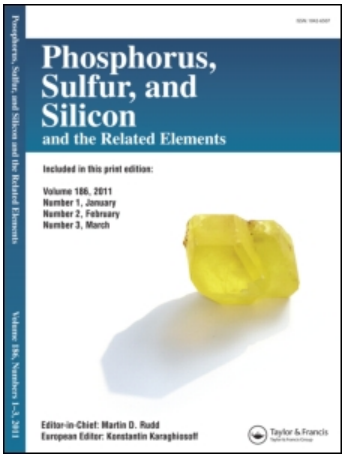

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SYNTHESIS OF 4-SUBSTITUTED (6-HYDROXY-2-HEXEN-1-YL)-DIPHENYLPHOSPHIN OXIDES AND THEIR APPLICATION TO THE HORNER-WITTIG REACTION

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SYNTHESIS OF 4-SUBSTITUTED (6-HYDROXY-2-HEXEN-1-YL)-DIPHENYLPHOSPHIN OXIDES AND THEIR APPLICATION TO THE HORNER-WITTIG REACTION

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Two (E)-(6-hydroxy-2-hexen-1-yl)diphenylophosphine oxides with one (**5**) or two (**6**) methyl groups at C-4 were synthesized from crotonaldehyde or 3-methyl-2-butenal. These phosphine oxides were used in the Horner-Wittig reaction with two aldehydes and three ketones. Two dienols obtained (**7c** and **7d**) are isomers of farnesol and geraniol, respectively.

Keywords: (2-Hydroxy-3-alkene-1-yl)diphenylphosphine oxides; (5-carbetoxy-2-alkene-1-yl) diphenylphosphine oxides; (6-hydroxy-2-alkene-1-yl)diphenylophosphine oxides; synthesis; claisen rearrangement; horner-wittig reaction

INTRODUCTION

Our interest in the Horner-Wittig reaction is connected with its application to the synthesis of isoprenoids. For this purpose we obtained diisopropyl (5-carbethoxy-4-methyl-2-hexen-1-yl)phosphonate as a potential synthon.[1] However, attempts to apply this phosphonate or diisopropyl (6-hydroxy-4-methyl-2-hexen-1-yl)phosphonate obtained from it to the Horner-Wadsworth-Emmons reaction with acetone were unsuccessful. They did not afford the expected prod-

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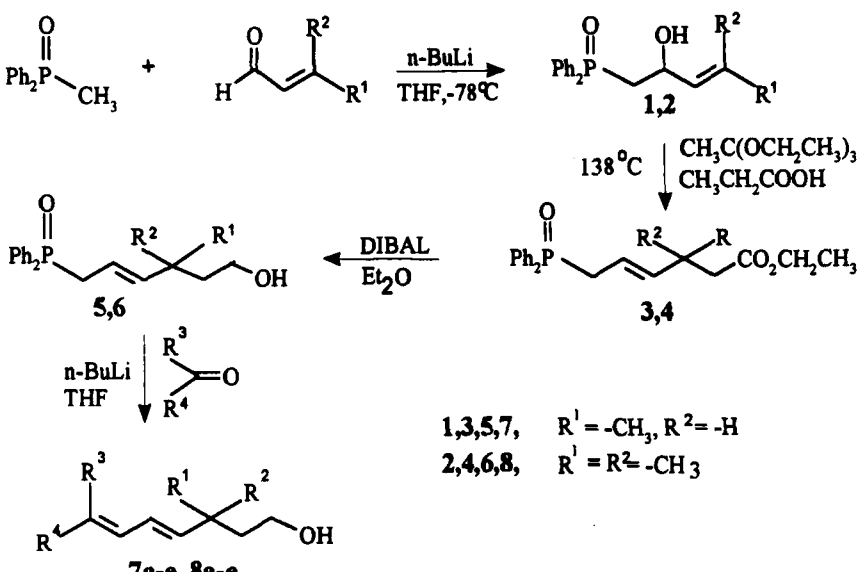
uct, 3.7-dimethyl-4,6-octadien-1-ol, in satisfactory yield. Thus, we decided to synthesize the diphenylphosphine oxides with the same alkene carbon unit and try to use them in the Horner-Wittig reaction. The allyl phosphine oxides were found as versatile synthons in the Horner-Wittig reaction[2–4].

RESULTS AND DISCUSSION

(4-Methyl-6-hydroxy-2-hexen-1-yl)diphenylphosphine oxide (**5**) and its 4,4-dimethyl homologue (**6**) were obtained in the three-step synthesis as outlined in the Scheme 1.

The first step, the condensation of lithiummethyldiphenylphosphine oxide with crotonaldehyde or with 3-methyl-2-butenal afforded in satisfactory yield the 1,2-addition products, allyl alcohols **1** (70%) and **2**, (75%) respectively.

The Claisen rearrangement, carried out according to the orthoacetate modification[5], transformed these alcohols into the corresponding γ,δ–unsaturated esters **3** and **4**. The double bond formed in the course of this reaction has the E (more than 97%, GC) configuration. The values of the coupling constants of the



a, R^3=-H, R^4 = $-C_6H_5$ b,R^3= -H,R^4 =$-C_5H_{11}$ c,R_3 =$-CH_3$, R^4 =$-CH_2CH_2CH=C(CH_3)_2$ d, R^3 =R^4 =$-CH_3$ e, R^3, R^4 =$-(CH_2)_5$-

SCHEME 1

olefinic protons H-2 and H-3 (J = 15.5 Hz for **3** and J = 15.7 Hz for **4**) and the presence of the absorption band at 970 cm^{-1} in the IR spectra prove the E configuration of this double bond.

The final (6-hydroxy-2-hexen-1-yl)diphenylphosphine oxides **5** and **6** were obtained in high yields (93 and 95%), by the reduction of esters **3** and **4** with diisobutyl aluminium hydride. The application of lithium borohydride for the reduction of **3** afforded diphenylphosphinoyl alcohol **5** but only in 65% yield.

The Horner-Wittig reaction of the dianions of hydroxyalkenylphosphine oxides **5** and **6** with two aldehydes (benzaldehyde and hexanal) and three ketones (acetone, cyclohexanone and 6-methyl-5-hepten-2-one) afforded the corresponding 4,6-dienols, **7a–e**, **8a–e** (Scheme 1). The reaction was carried out in tetrahydrofuran at −78°C (condensation) and 65°C (elimination) with the use of n-BuLi for a dianion generation. Lithium diisopropylamide (LDA) was also tried as a base for generation of dianion from **5** in the reaction with benzaldehyde but without any inacrease in the yield. The yields of the reaction were higher for aldehydes (80% for benzaldehyde and 75% for hexanal) than for ketones (only 50% for acetone). The olefination reactions of benzaldehyde with the dianions formed from phosphine oxide **5** as well as **6** were highly stereoselective and gave the newly formed double bond with the E configuration. This configuration is confirmed by the value of coupling constants between H-6 and H-7 (J = 15.6 Hz for **7a** and 15.7 Hz for **8a**). Thus, dienols **7a** and **8a** were obtained as 4E,6E isomers (above 95% according to GC).

Less stereoselective was the olefination reaction of hexanal. The mixture of 6Z and 6E isomers of the dienols **7b** (10% Z and 90% E) and **8b** (11% Z and 89% E) was identified as a product of the Horner-Wittig reaction of this aldehyde with the dianions derived from **5** and **6**, respectively.

Attempts to separate these mixtures by column chromatography were unsuccessful. ^1H NMR spectra recorded for **7b** and **8b** showed separate doublets (J = 6.8 Hz) at δ = 1.04 and 1.02 ppm for the methyl groups of the Z and E isomers of **7b**, respectively, and two singlets of the C-3 methyl groups at 1.06 and 1.04 ppm for the Z and E isomers of **8b**.

The isomeric mixtures of alcohols **7c** (30% of 4E, 6Z and 70% of 4E, 6E) and **8c** (28% of 4E, 6Z and 72% 4E, 6E) were obtained as products of the reaction of 6-methyl-5-hepten-2-one with the dianions derived from **5** or **6**, respectively. Alcohol **7c** is an isomer (position of the double bond) of the known, natural sesquiterpene alcohol, farnesol.

In these cases we partially separated, by column chromatography, the mixtures and we isolated small amount of pure 6Z isomers. Comparing the ^1H NMR spectra of pure 6Z isomers and those of mixture of isomers we were able to ascribe the signals of the protons to corresponding isomers. Different chemical shifts for

protons of the methyl groups at C-3, for H-4 olefinic proton, for protons of the methyl group at C-7 and for C-1 methylene protons were observed. A detailed analysis of ^{1}H NMR spectra is presented in the Experimental Part.

The single (4E) isomers, of dienoic alcohols **7d** and **7e** or **8d** and **8e** were isolated as products from the Horner-Wittig reactions of acetone and cyclohexanone with diphenylphosphine oxide **5** or **6**, respectively. The alcohol **7d** is an isomer of geraniol.

EXPERIMENTAL

Methyldiphenylphosphine oxide was synthesized from methyltriphenylphosphonium iodide according to Morgan and Herr[6]. All other reagents used in this work were purchased from Fluka. ^{1}H NMR spectra were recorded in solutions ($CDCl_3$ with c.a. 1% TMS) on Bruker Avance DRX 300 spectrometer. IR spectra were recorded on a Specord M-80 Carl Zeiss Jena Spectrometer. Analytical gas chromatography (GC) was performed on a Hewlett-Packard 5890 A II apparatus using HP-5 capilary column. Analytical thin layer chromatography (TLC) was carried out on silica gel G (Merck), various develping systems were applied. Compouds were detected by spraying the plates with 7% H_2SO_4 in ethanol containing c.a. 0.1% of p-anisaldehyde, followed by heating. Preparative column chromatography was carried out on silicagel gel 60 (230–400 mesh, Merck) with hexane-acetone, hexane-ethyl acetate or ethyl ether-acetone mixtures as an eluent. Melting points (uncorrected) were determined on Boetius apparatus.

(2-Hydroxy-3-Penten-1-yl)Diphenylphosphine Oxide (1)

n-Butyllithium (0.03 mol, 19 ml of 1.6M solution in hexane) was added dropwise to a solution of methyldiphenylphospine oxide (5.4g, 0.025 mol) in tetrahydrofuran (50 ml) under nitrogen at −78°C. After 15 min., crotonaldehyde (2.1 ml, 0.025 mol) was added dropwise at −78°C. The mixture was stirred for 20 min and then quenched with aqueous saturated solution of ammonium chloride (50 ml). Ethyl ether (50 ml) was added and the layers were separated. The aqueous layer was additionaly extracted with the ether (50 ml). The ethereal solution was washed with brine and dried ($MgSO_4$). The crude products were purified by column chromatography (ethyl ether—acetone, 6:1).

Pure hydroxy phosphine oxide **1** (5,4 g) was obtained in 75% yield, m.p. 100.5–102°C (lit[3] 102–103°C). ^{1}H NMR spectrum recorded on 300 MHz spectrometer allowed us to give its full interpretation; δ: 1.60 (d, J = 6.3 Hz, 3H,

=CH(C$\underline{H}_3$)), 2.47(ddd, J = 15.0, 8.4 and 3.0 Hz, 1H, -PC$\underline{H}_2$-), 2.66(ddd, J = 15.0, 10.6 and 9.7 Hz, 1H, -PC$\underline{H}_2$-), 4.45(s, 1H, -O$\underline{H}$), 4.50(m, 1H, -C$\underline{H}$(OH)-), 5.50(dd, J = 15.3 and 6.3Hz, 1H, -C$\underline{H}$=CH-CH_3), 5.65(dq, J = 15.3 and 6.3Hz, 1H, -CH=C$\underline{H}$-CH_3), 7.29–7.95 (m, 10H, $\underline{Ph}_2$PO).

(2-Hydroxy-4-Methyl-3-Penten-1-yl)Diphenylphosphine Oxide (2)

Analogously to the synthesis of **1** phosphine oxide, **2** (5.2 g, yield 70%) was obtained from 3-methyl-2-butenal (2.4 ml): m.p. 126–127°C, ^{1}H NMR, δ: 1.48 and 1.62 (two s, 6H, =C(C$\underline{H}_3$)$_2$), 2.37(ddd, J = 15.0, 6.9 and 2.5 Hz, 1H, PC$\underline{H}_2$-), 2.61 (ddd, J = 15.0, 11.3 and 9.9 Hz, 1H, PC$\underline{H}_2$-), 4.03 (s, 1H, -O$\underline{H}$), 4.83 (m, 1H, -C$\underline{H}$(OH)-), 5.28 (d, J = 8.3 Hz, 1H, -CH(OH)C$\underline{H}$=), 7.29–7.91(m, 10H, $\underline{Ph}_2$PO-); IR(cm^{-1}): 3390(s), 1640(w), 1440(s), 1196(w), 1120(s), 856(m). Anal. Calcd. for $C_{18}H_{21}O_2P$: C, 71.98; H, 7.05; P, 10.31. Found: C, 71.41; H, 7.22; P, 10.13.

(E)-(5-Carbethoxy-4-Methyl-2-Penten-1-yl)Diphenylphosphine Oxide(3)

A mixture of alcohol **1** (4.0g, 0.014 mol), ethyl orthoacetate (20 ml, 0.11 mol) and propionic acid (0.1 cm^3, 0.001 mol) was heated (138°C) for 6h with simultaneous distilling off the formed ethanol. Then orthoacetate was distilled off and the crude product was purified by column chromatography (hexane—acetone, 3:2). In this way pure **3** (4.6g, yield 92%) was obtained: m.p. 59,5–61°C; ^{1}H NMR, δ: 0.89 (d, 6.8 Hz, 3H, -CH(C$\underline{H}_3$)-), 1.21 (t, J = 7.1Hz, 3H, -OCH$_2$C$\underline{H}_3$), 2.11 (dd, J = 14.9 and 6.9 Hz, 1H, -C$\underline{H}_2$CO$_2$-), 2.17 (dd. J = 14.9 and 6.9Hz, 1H, -C$\underline{H}_2$CO$_2$-), 2.59 (m, 1H, -C$\underline{H}$(CH$_3$)-, 3.07 (m, 2H, -C$\underline{H}_2$CH=CH-), 4.06 (q, J = 7.1Hz, 2H, -OC$\underline{H}_2$CH$_3$), 5.40 (ddd, J = 15.5, 6.7 and 3.6Hz, 1H, −CH$_2$-CH=C$\underline{H}$-), 5.48 (dtd, J = 15.5, 6.5 and 4.5Hz, 1H, -CH$_2$C$\underline{H}$=CH-), 7.46–7.72 (m, 10H, P$\underline{h}_2$P); IR(cm^{-1}): 1732(s), 1680(m), 1440(m), 1192(m), 972(m). Anal. Calcd. for $C_{21}H_{25}O_3P$: C, 70.75; H, 7.07; P, 8.69. Found: C, 70.67; H, 7.11; P, 8.67.

(E)-(5-Carbethoxy-4,4-Dimethyl-2-Penten-1-yl)Diphenylphosphine Oxide (4)

Ester **4** (4,3 g, yield 90%) was obtained, from the alcohol **2** (4.0 g, 0.013 mol). Its physical and spectral data are as follows: m.p. 68.5–70°C; ^{1}H NMR, δ: 0.99 (s, 6H, -C(C$\underline{H}_3$)$_2$-), 1.23 (t, J = 7.1Hz, 3H, -OCH$_2$C$\underline{H}_3$), 2.15 (s, 2H, -C$\underline{H}_2$CO$_2$-), 3.10 (m, 2H, -C$\underline{H}_2$CH=CH-), 4.68 (q, J = 7.1Hz, 2H, -OC$\underline{H}_2$CH$_3$),

5.44 (dtd, J = 15.7, 7.0 and 5.1 Hz, 1H, -CH_2-C<u>H</u>=CH-), 5.56 (dd, J = 15.7 and 4.1 Hz, 1H, -CH_2-CH=C<u>H</u>-), 7.47–7.75 (m, 10H, P<u>h</u>$_2$P-); IR(cm^{-1}): 1792(s), 1640(m), 1440(m), 1188(m), 976(w). Anal. Calcd. for $C_{22}H_{27}O_3P$: C, 71.33; H, 7.35; P, 8.36. Found: C, 72.15; H, 7.42; P, 8.36.

(E)-(6-Hydroxy-4-Methyl-2-Hexen-1-yl)Diphenylphosphine Oxide (5)

Diisobutylaluminium hydride (15 ml of 1M solution in hexane, 0.015 mol) was added dropwise to a cooled (−78°C) solution of ester **3** (3.6 g, 0.012 mol) in ethyl ether (50 ml). Then the reaction mixture was slowly warmed up to room temperature and stirred for 6h. When the reaction was completed (TLC) the mixture was quenched at 0°C with saturated aqueous solution of ammonium chloride. The layers were separated and the aqueous layer was additionally extracted with ethyl ether. The combined ethereal solutions were washed with brine and dried ($MgSO_4$). Crude product was purified by column chromatography (ethyl ether—isopropyl alcohol, 20:1). Crystalline (recrystallisation from, ethyl ether, m.p. 69–70°C) phosphine oxide **5** (3.6 g, yield 95%) was obtained: ^{1}H NMR, δ: 0.88 (d, J = 6.7 Hz, 3H, -CH(C<u>H</u>$_3$)-), 1.31–1.53 (m, 2H, -C<u>H</u>$_2$$CH_2$OH), 2.2 (m, 1H, -C<u>H</u>(CH_3)-), 2.54(s, 1H, -O<u>H</u>), 3.03–3.10 (m, 2H, -PC<u>H</u>$_2$-), 3.43 (t, J = 6.2Hz, 2H, -C<u>H</u>$_2$OH), 5.36–5.42 (m, 2H, -C<u>H</u>=C<u>H</u>-), 7.46–7.76 (m, 10H, P<u>h</u>$_2$P-); IR (cm^{-1}): 3510(s), 1670(w), 1440(s), 1192(s), 1120(s), 975(m). Anal. Calcd. for $C_{19}H_{23}O_2P$: C, 72.59; H, 7.37; P, 9.85. Found: C, 72.42; H, 7.31; P, 9.81.

(E)-(6-Hydroxy-4,4-Dimethyl-2-Hexen-1-yl)Diphenylphosphine Oxide (6)

According to the procedure described above, (hydroxyalkyl)diphenyl- phosphine oxide **6** (3.7 g, yield 93%) was obtained from the reduction of phosphine oxide **4** (4.0 g, 0.012 mol) as crystalline product. Recrystalisation from ethyl ether gave pure **6**, m.p. 88–90°C; ^{1}H NMR, δ: 0.89 (s, 6H, -C(C<u>H</u>$_3$)$_2$-), 1.5 (t, J = 6.5 Hz, 2H, -C<u>H</u>$_2$-CH_2OH), 2.76 (s, 1H, -O<u>H</u>), 3.07 (dd, J = 13.7 and 7.4 Hz, 2H, -PC<u>H</u>$_2$), 3.45 (t, J = 6.5 Hz, 2H, -C<u>H</u>$_2$OH), 5.24 (dtd, J = 15.7, 7.4 and 5.2 Hz, 1H, -CH_2C<u>H</u> = CH-), 5.62 (dd, J = 15.7 and 4.7 Hz, 1H, -CH_2CH=C<u>H</u>-), 7.46–7.74 (m, 10H, P<u>h</u>$_2$P-); IR (cm^{-1}): 3332 (s,b), 1640(w), 1440(s), 1192(s), 1048(s), 976(m). Anal. Calcd. for $C_{20}H_{25}O_2P$: C, 73.15; H, 7.67; P, 9.43. Found: C, 73.97; H, 8.09; P, 9.53.

Synthesis of Alcohols 7a–e and 8a–e

General procedure: To a cooled (−78°) solution of phosphine oxide **5** or **6** (0.0011 mol) in anhydrous tetrahydrofuran (50 ml), n-butyllithium (1.5 ml of

1,6M solution in hexane, 0.0024 mol) was added dropwise under nitrogen. After 5 min the appropriate carbonyl compound (0.0011 mol) in tetrahydrofuran (10 ml) was added. The reaction mixture was warmed up to a room temperature and after next 0.5 h was heated at 65°C. The course of the reaction was monitored by TLC. When the reaction was completed a saturated aqueous solution of ammonium chloride (10 ml) was added and the product was extracted with ethyl ether (3 × ml 50 ml). The ethereal solution was washed with brine and dried ($MgSO_4$). Ether was removed under reduced pressure and the residue was subjected to column chromatography (hexane-acetone, 10:1).

The reaction yields, physical and spectral data of alcohols **7a–e** and **8a–e** are as follows:

(4E, 6E)-3-Methyl-7-Phenyl-4,6-Heptadien-1-ol (7a): yield 92%; b.p. 140–141°C/2.5 mmHg; n_D^{20} = 1.5820; ^{1}H NMR, δ: 1.08 (d, J = 6.7 Hz, 3H, -CH(C<u>H</u>$_3$)-), 1.60 (m, 2H,-C<u>H</u>$_2$CH$_2$OH), 2.41–2.65 (m, 1H, -C<u>H</u>(CH$_3$)-, and s, 1H, -O<u>H</u>), 3.65 (t, J = 7.2 Hz, 2H, -C<u>H</u>$_2$OH), 5.71 (dd, J = 15.2 and 8.1 Hz, 1H, H-4), 6.22(dd, J = 15.2 and 10.6 Hz, 1H, H-5), 6.46 (d, J = 15.7, 1H, H-7), 6.74(dd, J = 15.7 and 10.6Hz, 1H, H-6), 7.35–7.61 (m, 5H, C$_6$<u>H</u>$_5$-); IR (cm^{-1}): 3344 (s), 1596(w), 1448 (m), 1048 (s), 992 (s), 750 (s), 700 (s); Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12;H, 8.97. Found: C, 82.97; H, 8.89.

3-Methyl-4,6-dodecadien-1-ol (7b, mixture of isomers 4E, 6Z-10% and 4E, 6E-0 90%): yield 79%, b.p. 105°C/3 mmHg; ^{1}H NMR, δ: 0.86 (t, J = 6.4 Hz, 3H, -CH$_2$C<u>H</u>$_3$), 1.02 (d, J = 6.7Hz, -CH(C<u>H</u>$_3$)-, isomer 6E), 1.04 (d, J = 6.7 Hz, -CH(C<u>H</u>$_3$)-, isomer 6Z), 1.25–1.45 (m, 7H, -(C<u>H</u>$_2$)$_3$CH$_3$, -O<u>H</u>), 1.57 (m, 2H, -C<u>H</u>$_2$CH$_2$OH), 2.06 (m, 2H, -C<u>H</u>$_2$CH═), isomer 6E), 2.15 (m, 2H, -C<u>H</u>$_2$CH═, isomer 6Z), 2.32 (m, 1H, -C<u>H</u>(CH$_3$)-), 3.65 (t, J = 6.5 Hz, 2H, -C<u>H</u>$_2$OH), 5.40–5.62 (m, 2H, H-6 and H-7), 5.95–6.05 (m, 2H, H-4 and H-5); IR (cm^{-1}): 3392(s,b), 1260(s), 1048 (s), 991 (s). Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.35; H, 12.27.

3,7,11-Trimethyl-4,6,10-Dodecatrien-1-ol (7c, mixture of 30% of isomers 4E, 6Z and 70% of isomers 4E, 6E): yield 62%; b.p. 108–109°C/3 mmHg; ^{1}H NMR, δ: 1.03 (d, J = 6.7Hz, 3H, -CH(C<u>H</u>$_3$)-, isomer 6Z), 1.04 (d, J = 6.7Hz, 3H, -CH(C<u>H</u>$_3$)-, isomer 6E), 1.53–1.63 (m, 3H, -C<u>H</u>$_2$CH$_2$OH, -O<u>H</u>), 1.61 and 1.69 (two s, 6H, ═C(C<u>H</u>$_3$)$_2$), 1.74 (s, 3H, -(C<u>H</u>$_3$)C═, isomer 6E), 1.76 (s, 3H, -(C<u>H</u>$_3$)C═, isomer 6Z), 2.03–2.14 (m, 4H, -C<u>H</u>$_2$C<u>H</u>$_2$CH═), 2.36 (m, 1H, -C<u>H</u>(CH$_3$)-, 3.65 (t, J = 6.6Hz, 2H, -C<u>H</u>$_2$OH, isomer 6Z), 3.66 (t, J = 6.6Hz, 3H, -C<u>H</u>$_2$OH, isomer 6E), 5.10 (m, 1H, H-10, isomer 6E), 5.13 (m, 1H, H-10, isomer 6Z), 5.44 (dd, J = 15.1 and 8.2Hz, 1H, H-4, isomer 6Z), 5.46 (dd, J = 15.2 and 8.1Hz, 1H, H-4, isomer 6E), 5.79 (d, J = 10.9Hz for 6Z and J = 10.8Hz for 6E, 1H, H-6), 6.24 (dd, J = 15.1 and 10.9Hz, 1H, H-5, isomer 6Z),

6.25 (dd, J = 15.2 and 10.8Hz, 1H, H-5, isomer 6E); IR (cm^{-1}): 3376(s,b), 1616(w), 1380(s). 1024 (s), 968 (s). Anal. Calcd. for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found: C, 79.82; H, 12.35.

(E)-3,7-Dimethyl-4,6-Octadien-1-ol (7d): yield 55%; b.p. 74–75°C/3 mmHg, n_D^{20} = 1.4655; ^1H NMR, δ: 0.96 (d, J = 6.9Hz, 3H, -CH(C$\underline{H}_3$)-), 1.62 (m, 2H, -C$\underline{H}_2$CH$_2$OH), 1.67 (s, 6H, =C(C$\underline{H}_3$)$_2$), 1.80 (s, 1H, -O$\underline{H}$), 3.58 (t, J = 6.6Hz, 2H, -C$\underline{H}_2$OH), 5.35 (dd, J = 14.9 and 8.0Hz, 1H, H-4), 5.70 (d, J = 10.5Hz, 1H, H-6), 6.17 (dd, J = 14.9 and 10.5Hz, 1H, H-5); IR (cm^{-1}): 3440 (s,b), 1664 (m), 1372 (s), 1160 (s), 960 (s). Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.67; H, 11.29.

(E)-3-Methyl-6-Cyclopentylidene-4-Hexen-1-ol (7e): yield 70%; b.p. 115–116°C/2,5 mmHg; n_D^{20} = 1.5146; ^1H NMR, δ: 1.03 (d, J = 6.6Hz, 3H, -CH(C$\underline{H}_3$)-), 1.25–2.45 (m, 14H, -(C$\underline{H}_2$)$_5$- groups, -C$\underline{H}$(CH$_3$)- and -C$\underline{H}_2$CH$_2$O$\underline{H}$), 3.65 (t, J = 6.5Hz, 2H, -C$\underline{H}_2$OH), 5.44 (dd, J = 14.9 and 8.0Hz, 1H, H-4), 5.72 (d, J = 10.8Hz, 1H, H-7), 6.30 (dd, J = 14.9 and 10.8Hz, 1H, H-5); IR (cm^{-1}): 3384 (s), 1616 (w), 1380 (s), 1052 (s), 968 (s). Anal. Calcd. for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.09; H, 11.45.

(4E,6E)-3,3-Dimethyl-7-Phenyl-4,6-Heptadien-1-ol (8a): yield 85%; b.p. 148–149°C/3 mmHg; n_D = 1.5606; ^1H NMR, δ: 1.08 (s, 6H, -C(C$\underline{H}_3$)$_2$-), 1.67 (t, J = 7.2Hz, 2H, -C$\underline{H}_2$CH$_2$OH), 2.61 (s, 1H, -O$\underline{H}$), 3.66 (t, J = 7.2Hz, 2H, -C$\underline{H}_2$OH), 5.83 (d, J = 15.6Hz, 1H, H-4), 6.15 (dd, J = 15.6 and 10.2Hz, 1H, H-5), 6.48 (d, J = 15.5Hz, 1H, H-7), 6.75 (dd, J = 15.5 and 10.2Hz, 1H, H-6), 7.20–7.40 (m, 5H, C$_6$-H$_5$-); IR (cm^{-1}): 3344 (s,b), 3024 (m), 1496 (m), 1472 (m), 1024 (s), 992 (s), 748 (s), 696 (s). Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.31. Found: C, 84.48; H, 9.42.

3,3-Dimethyl-4,6-Dodecadien-10-ol (8b, mixture of 11% of isomers 4E, 6Z and 89% of 4E, 6E): yield 91%; b.p. 108–109°C/3 mmHg; ^1H NMR, δ: 0.89 (t, J = 6.9Hz, -CH$_2$C$\underline{H}_3$), 1.04 (s, 6H, -C(C$\underline{H}_3$)$_2$-, isomer 6E), 1.06 (s, 6H, -C(C$\underline{H}_3$)$_2$-, isomer 6Z), 1.25–1.36 (m, 6H, -C$\underline{H}_2$- groups and s, 1H, -O$\underline{H}$), 1.62 (t, J = 7.2Hz, 2H, -C$\underline{H}_2$-CH$_2$-OH), 2.05 (m, 2H, -C$\underline{H}_2$-CH=, isomer 6E), 2.16 (m, -C$\underline{H}_2$CH=, isomer 6Z), 3.62 (t, J = 7.2Hz, 2H, -CH$_2$OH, isomer 6Z), 3.64 (t, J = 7.2Hz, -C$\underline{H}_2$OH, isomer 6E), 5.54–5.68 (m, 2H, -C$\underline{H}$=C$\underline{H}$-C(CH$_3$)$_2$-), 5.90–6.04 (m, 2H, -CH$_2$C$\underline{H}$=C$\underline{H}$-); IR (cm^{-1}): 3336 (s,b), 1616 (w), 1456 (s), 1024 (s), 992 (s). Anal. Calcd. for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found: C, 80.01; H, 12.58.

3,3,7,11-Tetramethyl-4,6,10-Dodecatrien-1-ol (8c, mixture of 28% of isomers 4E, 6Z and 72% of isomers 4E, 6E): yield 63%; b.p. 126–127°C/4 mmHg; ^1H NMR, δ: 1.05 (s, 6H, -C(C$\underline{H}_3$)$_2$-, isomer 6Z), 1.07 (s, 6H, -C(C$\underline{H}_3$)$_2$-, isomer 6E), 1.25 (s, 1H, -O$\underline{H}$), 1.61 (s, 3H, CH$_3$-7, isomer 6E), 1.62 (s, 3H, CH$_3$-7, isomer 6Z), 1.63 (t, J = 7.2Hz, 2H, -C$\underline{H}_2$CH$_2$OH), 1.69 and 1.75 (two s, 6H,

=C(C$\underline{H}_3$)$_2$), 2.08–2.17 (m, 4H, =CHC$\underline{H}_2$C$\underline{H}_2$-), 3.64 (t, J = 7.2Hz, 2H, -C$\underline{H}_2$OH, isomer 6Z), 3.65 (t, J = 7.2Hz, 2H, -C$\underline{H}_2$OH, isomer 6E), .5.13 (m, 1H, H-10), 5.56 (d, J = 15.4Hz, H-4, isomer 6Z), 5.59 (d, J = 15.4Hz, H-4, isomer 6E), 5.80 (d, J = 10.6Hz, 1H, H-6), 6.18 (dd, J = 15.4 and 10.6Hz, H-5). IR(cm^{-1}): 3376 (s,b), 1616 (m), 1448 (s), 1024 (s), 968 (s). Anal. Calcd. for $C_{15}H_{28}O$: C, 81.29; H, 11.94. Found: C, 81.04; H, 12.13.

(E)-3,3,7-Trimethyl-4,6-Octadien-1-ol (8d): yield 50%; b.p. 72–73°C/2,5 mmHg; n_D^{20} = 1.4879; ^{1}H NMR, δ: 1.06 (s, 6H, -C(C$\underline{H}_3$)$_2$-), 1.62 (t, J = 7.0Hz, 2H, -C$\underline{H}_2$CH$_2$OH), 1.75 and 1.76 (two s, 6H, =C(C$\underline{H}_3$)$_2$), 2.25 (s, 1H, -O$\underline{H}$), 3.65 (t, J = 7.0Hz, 2H, -C$\underline{H}_2$OH), 5.55 (d, J = 15.4Hz, 1H, H-4), 5.74 (d, J = 10.5Hz, 1H, H-6), 6.19 (dd, J = 15.4 and 10.5Hz, 1H, H-5); IR (cm^{-1}): 3372 (s,b), 1624 (w), 1264 (s), 1024 (s). Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.32; H, 11.82.

(E)-3,3-Dimethyl-6-Cyclopentylidene-4-Hexen-1-ol (8e): yield 63%; b.p. 120–121 °C/3 mmHg; n_D^{20} = 1.5197; ^{1}H NMR, δ: 1.06 (s, 6H, -C(C$\underline{H}_3$)$_2$-), 1.25–1.85 (m, 8H, -(CH$_2$)$_3$-, -C$\underline{H}_2$CH$_2$OH), 1.9 (s, 1H, -O$\underline{H}$), 2.0–2.4 (m, 4H, -(C$\underline{H}_2$)$_2$C=), 3.66 (t, J = 7.2Hz, C$\underline{H}_2$OH), 5.58 (d, J = 15.4Hz, 1H, H-4), 5.73 (d, J = 10.0Hz, 1H, H-5), 6.24 (dd, J = 15.4 and 10.0Hz, 1H, H-5); IR (cm^{-1}): 3392 (s,b), 1616 (w), 1448 (s), 1024 (s), 968 (s). Anal. Calcd. for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.35; H, 11.43.

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