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Samarium(II)-mediated reaction of allylic phosphate esters with carbonyl compounds: A new method for "Umpolung" of allylic phosphates

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Abstract

Allylic phosphates allylate ketones and aldehydes in the presence of samarium(II) iodide. The coupling proceeds with the preservation of the olefin geometry, however, regio- and stereoselectivity are not high.

Introduction

The use of allylic phosphate esters in the field of synthetic organic chemistry has over the past two decades been extensively developed [1]. This tendency is, of course, closely related to the fact that naturally occurring terpenoids are biosynthesized regio- and stereospecifically via allylic pyrophosphate esters [2]. Allylic phosphates have been found to possess several advantages over allylic halides in regard to reactivity, selectivity, and ease of preparation and handling [1]. However, allylic phosphates have been hitherto used as allylic cation equivalents and little effort has been directed at their use as allylic anion synthons. Nozaki and coworkers recently reported the successful allylation of aldehydes by allylic phosphates using chromium(II) [3] and aluminum-tin combined reagents [4]. Here we describe the results of the samarium(II)-mediated coupling of allylic phosphates and carbonyl compounds which provides a new method for "Umpolung" of allylic phosphates.

Results and discussion

In 1980, Kagan reported the preparation of Sm^{II} iodide by the reaction of Sm metal and 1,2-diiodoethane in tetrahydrofuran (THF) and found that this reagent is useful for Barbier–Grignard type coupling of organic halides and sulfonates with carbonyl compounds [5]. We have now examined this reagent for the cross-coupling of allylic phosphates with various carbonyl compounds. The reactions were con-

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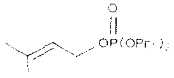
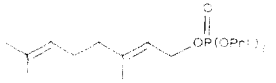
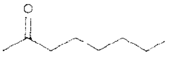
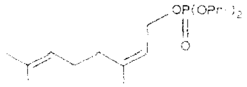
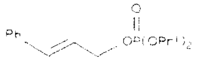
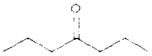
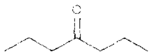
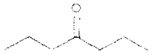
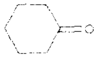
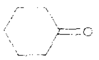
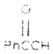
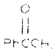
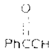
Table 1

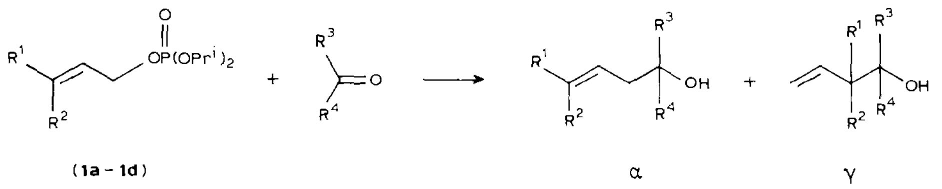
Sm^{II}-mediated reaction of allylic phosphates and carbonyl compounds

Entry	Carbonyl compound	Allylic phosphate	Coupling product Yield (%) (α : γ)	Pinacol Yield (%)
1		 (1a)	93 (64 : 36)	–
2		 (1b)	79 (65 : 35)	–
3		 (1c)	75 (68 : 32)	–
4		 (1d)	69 (60 : 40)	–
5		**1a**	69 (60 : 40)	–
6		**1b**	65 (63 : 37)	–
7		**1d**	65 (44 : 56)	–
8		**1a**	66 (66 : 34) [a]	–
9		**1b**	56 (63 : 37)	–
10		**1d**	37 [b] (70 : 30)	–
11	 $PhC(=O)CH_3$	**1a**	14 (58 : 42)	81
12	 $PhC(=O)CH_3$	**1b**	10 (50 : 50)	90 [c]
13	 $PhC(=O)CH_3$	**1d**	17 (29 : 71)	83 [c]
14		**1a**	41 (37 : 63)	51
15		**1b**	38 (38 : 62)	67 [c]
16		**1d**	23 (71 : 29)	70 [c]
17	PhCHO	**1a**	–	80

[a] By glc. [b] Phosphate was recovered (37%). [c] Yield of crude material.

ducted in THF at room temperature using Sm^{II}, allylic phosphate, and carbonyl compound in the ratio of 2 : 1 : 1.5. The reactions usually went to completion within one hour. The products were purified by column chromatography on silica gel and the structures were deduced from their analytical and spectral data. Results are listed in Table 1.

Aliphatic and alicyclic ketones such as 2-octanone, 4-heptanone, and cyclohexanone reacted with allylic phosphates (**1a–d**) to give coupling products in good



to moderate yields. The reactions of acetophenone afforded pinacol along with poor yields of the cross-coupling products. Octanal (aliphatic aldehyde) also gave the coupled alcohols, along with considerable amounts of the pinacol. However, the reaction of benzaldehyde (aromatic aldehyde) with prenyl phosphate (**1a**) gave only 1,2-diphenyl-1,2-ethanediol in 80% yield with no cross-coupling products. α,β-Unsaturated carbonyl compounds such as 2-cyclohexenone, mesityl oxide, and 3-methyl-2-butenal all gave complex mixtures of products. Methyl octanoate and octyl cyanide were not allylated by this method. Diisopropyl 3-methyl-3-butenyl phosphate (homoallylic phosphate) did not react with 2-octanone, even under rigorous conditions (THF reflux, 18 h).

As shown in Table 1, the present coupling lacks regioselectivity, so the coupling products are a mixture of the products coupled at either the α- and γ-positions of the allylic phosphates. Furthermore, the γ-coupling products from the reactions of 2-octanone, acetophenone, and octanal are all mixtures of diastereomers (*erythro* and *threo* ca. 1 : 1). However, the geometry of the allylic double bond is completely preserved. Thus, the products from geranyl phosphate (**1b**) retain the original *E* geometry and those from neryl phosphate (**1c**) keep the *Z* geometry.

Although the reactions of the allylic phosphates described above are essentially the same as those of allylic halides [5], the present method is a unique example of the use of allylic phosphates as allylic anion equivalents.

Experimental

IR spectra were recorded with a JASCO A-102 spectrometer. ^1H NMR spectra were recorded with a Hitachi R-24A (60 MHz) or a Varian XL-200 (200 MHz) spectrometer. The chemical shifts are given in δ with tetramethylsilane as an internal standard. Mass spectra were run with a Hitachi M-52 instrument at 20 eV. GLC analyses were performed on a Yanaco G 1800 gas chromatograph equipped with a column (1 m × 3 mm) packed with 5% polyethylene glycol (PEG-20M P) on Uniport HP. Boiling points refer to bath temperature during Kugelrohr distillation (Shibata GTO-250R). Elemental analyses were performed at the Elemental Analysis Center of Kyoto University. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl. All the reactions were carried out under nitrogen.

Sm^{II}-mediated reaction of allylic phosphate with carbonyl compound

The following reaction of diisopropyl prenyl phosphate (**1a**) with 2-octanone (entry 1) is representative. To a solution of samarium(II) iodide, which had been prepared by a published procedure [5] from samarium metal (325 mg, 2.16 mmol) and 1,2-diiodoethane (360 mg, 1.28 mmol) in THF (20 ml), was added a mixture of **1a** (127 mg, 0.51 mmol) and 2-octanone (100 mg, 0.78 mmol) in THF (1 ml) at room temperature. The mixture was stirred for 1 h and then quenched by the addition of diluted (0.5 *N*) hydrochloric acid. The products were extracted with ether. The extracts were successively washed with water, aqueous $Na_2S_2O_3$, water, and brine and then dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (benzene as eluant) to give 2,5-dimethyl-2-undecen-5-ol (60 mg, 60%) and 3,3,4-trimethyl-1-decen-4-ol (34 mg, 33%).

All other experiments were carried out similarly, and the products were isolated by column chromatography on silica gel. However, separation of the products for entry 8 was performed by preparative glc.

2,5-Dimethyl-2-undecen-5-ol. See ref. 5.

3,3,4-Trimethyl-1-decen-4-ol. See ref. 5.

(E)-7,10,14-Trimethyl-9,13-pentadecadien-7-ol. B.p. 115 °C/2 Torr; Found: C, 81.05; H, 13.13. $C_{18}H_{34}O$ calc: C, 81.14; H, 12.86%. IR (neat): 3420, 2970, 2940, 2890, 2870, 1662, 1450, 1378, 1110, 935, 900 cm^{-1}; ^1H NMR ($CDCl_3$): 0.89 (bt, *J* 6 Hz, 3H, Me), 1.15 (s, 3H, Me), 1.20–1.58 (m, 11H, CH_2 and OH), 1.62 (s, 3H, Me), 1.64 (s, 3H, Me), 1.69 (s, 3H, Me), 2.04–2.23 (m, 6H, CH_2), 5.10 (m, 1H, olefin H), 5.23 (t, *J* 8 Hz, 1H, olefin H); MS: *m/z* (rel. intensity) 248 ($M^+ - H_2O$, 1), 138 (48), 129 (91), 123 (58), 95 (100), 69 (78).

2,6,7-Trimethyl-6-vinyl-2-tridecen-7-ol. B.p. 115 °C/2 Torr; Found: C, 80.91; H, 13.10. $C_{18}H_{34}O$ calc: C, 81.14; H, 12.86%. IR (neat) 3500, 3090, 2970, 2940, 2875, 1635, 1460, 1418, 1379, 1262, 1084, 1017, 914, 802 cm^{-1}; ^1H NMR ($CDCl_3$): 0.88 (bt, *J* 6 Hz, 3H, Me), 1.02 and 1.04 (each s, 3H, Me), 1.09 and 1.11 (each s, 3H, Me), 1.15–1.56 (m, 13H, CH_2 and OH), 1.59 (s, 3H, Me), 1.68 (s, 3H, Me), 1.74–1.97 (m, 2H, CH_2), 5.05 (dd, *J* 18, 2 Hz, 1H, olefin H), 5.13 (bt, *J* 7 Hz, 1H, olefin H), 5.24 (dd, *J* 11, 2 Hz, 1H, olefin H), 5.91 and 5.92 (each dd, *J* 18, 11 Hz, 1H, olefin H); MS: *m/z* (rel. intensity) 248 ($M^+ - H_2O$, 1), 166 (16), 138 (20), 129 (95), 95 (100), 69 (91).

(Z)-7,10,14-Trimethyl-9,13-pentadecadien-7-ol. B.p. 158 °C/5 Torr; Found: C, 81.37; H, 12.93. $C_{18}H_{34}O$ calc: C, 81.14; H, 12.86%. IR (neat): 3370, 2975, 2940, 2870, 1452, 1375, 1140, 1109, 1094, 1060, 932, 898 cm^{-1}; ^1H NMR ($CDCl_3$): 0.89 (bt, *J* 6 Hz, 3H, Me), 1.15 (s, 3H, Me), 1.27–1.51 (m, 11H, CH_2 and OH), 1.62 (s, 3H, Me), 1.69 (s, 3H, Me), 1.75 (s, 3H, Me), 2.05–2.10 (m, 4H, CH_2), 2.18 (d, *J* 8 Hz, 2H, CH_2), 5.08–5.18 (m, 1H, olefin H), 5.25 (t, *J* 8 Hz, 1H, olefin H); MS: *m/z* (rel. intensity) 251 ($M^+ -$ Me, 1), 248 ($M^+ - H_2O$, 8), 233 ($M^+ -$ Me $- H_2O$, 1), 138 (36), 129 (75), 123 (45), 95 (100), 69 (77).

(E)-4-Methyl-1-phenyl-1-decen-4-ol. See ref. 5.

4-Methyl-3-phenyl-1-decen-4-ol. See ref. 5.

7-Methyl-4-propyl-6-octen-4-ol. See ref. 6.

3,3-Dimethyl-4-propyl-1-hepten-4-ol. See ref. 6.

(E)-7,11-Dimethyl-4-propyl-6,10-dodecadien-4-ol. B.p. 145–153 °C/4.9 Torr; Found: C, 80.84; H, 12.75. $C_{17}H_{32}O$ calc: C, 80.88; H, 12.78%. IR (neat): 3420, 2970, 2930, 2880, 2870, 1664, 1463, 1450, 1374, 1148, 1130, 1108, 979, 903, 869, 742

cm^{-1}; ^1H NMR ($CDCl_3$): 0.91 (t, J 6 Hz, 6H, Me), 1.23–1.46 (m, 9H, CH_2 and OH), 1.60 (s, 3H, Me), 1.62 (s, 3H, Me) 1.68 (s, 3H, Me), 2.06–2.19 (m, 6H, CH_2), 5.03–5.15 (m, 1H, olefin H), 5.20 (t, J 7 Hz, 1H, olefin H); MS: m/z (rel. intensity) 234 ($M^+ - H_2O$, 2), 209 (4), 138 (26), 123 (35), 115 (100), 95 (45), 69 (30).

5,9-Dimethyl-4-propyl-5-vinyl-8-decen-4-ol. B.p. 153°C/5.1 Torr; Found: C, 81.05; H, 12.86. $C_{17}H_{32}O$ calc: C, 80.88; H, 12.78%. IR (neat): 3520, 3080, 2970, 2930, 2880, 1630, 1462, 1452, 1411, 1375, 1112, 1013, 986, 910, 745 cm^{-1}; ^1H NMR ($CDCl_3$) 0.90 (t, J 6 Hz, 6H, Me), 1.26–1.58 (m, 11H, CH_2 and OH), 1.60 (s, 3H, Me), 1.69 (s, 3H, Me), 1.73–1.92 (m, 2H, CH_2), 5.04 (dd, J 17, 1 Hz, 1H, olefin H), 5.11 (bt, J 6 Hz, 1H, olefin H), 5.20 (dd, J 11, 1 Hz, 1H, olefin H), 5.94 (dd, J 17, 11 Hz, 1H, olefin H); MS: m/z (rel. intensity) 234 ($M^+ - H_2O$, 1), 209 (4), 138 (7), 123 (16), 115 (100), 95 (32), 71 (18), 69 (24).

(E)-1-Phenyl-4-propyl-1-hepten-4-ol. See ref. 7.

3-Phenyl-4-propyl-1-hepten-4-ol. B.p. 142–150°C/2.8 Torr; Found: C, 82.68; H, 10.56. $C_{16}H_{24}O$ calc: C, 82.70; H, 10.41%. IR (neat): 3480, 3075, 3030, 2970, 2940, 2875, 1638, 1600, 1494, 1464, 1452, 1378, 1134, 996, 910, 736, 700 cm^{-1}; ^1H NMR ($CDCl_3$): 0.80 (t, J 6 Hz, 3H, Me), 0.96 (t, J 6 Hz, 3H, Me), 1.15–1.58 (m, 9H, CH_2 and OH), 3.33 (d, J 10 Hz, 1H, CH), 5.09 (dd, J 17, 1 Hz, olefin H), 5.15 (dd, J 10, 1 Hz, 1H, olefin H), 6.35 (ddd, J 17, 10, 10 Hz, 1H, olefin H), 7.22–7.40 (m, 5H, Ph); MS: m/z (rel. intensity) 214 ($M^+ - H_2O$, 1), 118 (69), 115 (100), 71 (20), 55 (20).

1-(3-Methyl-2-butenyl)cyclohexanol. See ref. 8.

1-(1,1-Dimethyl-2-propenyl)cyclohexanol. See ref. 9.

(E)-1-(3,7-Dimethyl-2,6-octadienyl)cyclohexanol. B.p. 120–150°C/2 Torr; Found: C, 81.31; H, 12.21. $C_{16}H_{28}O$ calc: C, 81.29; H, 11.94%. IR (neat): 3400, 2970, 2930, 2870, 1665, 1448, 1375, 1265, 1150, 972, 960, 890, 850, 834 cm^{-1}; ^1H NMR (CCl_4): 1.21–1.50 (m, 10H, CH_2), 1.50–1.71 (m, 10H, Me and OH), 1.93–2.15 (m, 6H, CH_2), 4.88–5.09 (m, 1H, olefin H), 5.15 (t, J 8 Hz, 1H, olefin H); MS: m/z (rel. intensity) 218 ($M^+ - H_2O$, 1), 138 (39), 123 (40), 99 (100), 95 (76), 81 (33), 69 (51).

1-(1,5-Dimethyl-1-vinyl-4-hexenyl)cyclohexanol. B.p. 120–150°C/2 Torr; Found: C, 81.11; H, 12.22. $C_{16}H_{28}O$ calc: C, 81.29; H, 11.94%. IR (neat): 3500, 3080, 2940, 2865, 1633, 1450, 1415, 1376, 1348, 1259, 1125, 1043, 1012, 964, 911, 840 cm^{-1}; ^1H NMR (CCl_4): 1.02 (s, 3H, Me), 1.26–1.65 (m, 13H, CH_2 and OH), 1.59 (s, 3H, Me), 1.69 (s, 3H, Me), 1.73–1.90 (m, 2H, CH_2), 5.04 (dd, J 18, 2 Hz, 1H, olefin H), 5.13 (bt, J 8 Hz, 1H, olefin H), 5.23 (dd, J 11, 2 Hz, 1H, olefin H), 5.89 (dd, J 18, 11 Hz, 1H, olefin H); MS: m/z (rel. intensity) 218 ($M^+ - H_2O$, 1), 138 (21), 123 (42), 99 (100), 95 (86), 81 (33), 69 (73).

(E)-1-(3-Phenyl-2-propenyl)cyclohexanol. See ref. 10.

1-(1-Phenyl-2-propenyl)cyclohexanol. See ref. 10.

5-Methyl-2-phenyl-4-hexen-2-ol. B.p. 90–100°C/5 Torr; Found: C, 82.16; H, 9.63. $C_{13}H_{18}O$ calc: C, 82.06; H, 9.53%. IR (neat): 3440, 2970, 2930, 1495, 1445, 1375, 1260, 1085, 1063, 1025, 945, 872, 760, 698 cm^{-1}; ^1H NMR ($CDCl_3$): 1.54 (s, 3H, Me), 1.62 (s, 3H, Me), 1.68 (s, 3H, Me), 1.42–1.76 (m, 1H, OH), 2.56 (d, J 8 Hz, 2H, CH_2), 5.03 (t, J 8 Hz, 1H, olefin H), 7.23–7.56 (m, 5H, Ph); MS: m/z (rel. intensity) 172 ($M^+ - H_2O$, 1), 122 (10), 121 (100), 70 (11), 43 (35).

3,3-Dimethyl-2-phenyl-4-penten-2-ol. B.p. 90–100°C/5 Torr; Found: C, 81.76; H, 9.57. $C_{13}H_{18}O$ calc: C, 82.06, H, 9.53%. IR (neat): 3470, 3070, 3060, 2970, 2875, 1675, 1445, 1372, 1175, 1070, 1024, 1009, 908, 757, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$): 0.99 (s, 3H, Me), 1.03 (s, 3H, Me), 1.59 (s, 3H, Me), 1.62–1.80 (m, 1H, OH), 5.06 (dd, J 18, 2 Hz, 1H, olefin H), 5.14 (dd, J 10, 2 Hz, 1H, olefin H), 5.97 (dd, J 18, 10 Hz, 1H, olefin H), 7.26–7.49 (m, 5H, Ph); MS: m/z (rel. intensity) 122 (10), 121 (100), 43 (36).

(E)-5,9-Dimethyl-2-phenyl-4,8-decadien-2-ol. B.p. 150–160 °C/5 Torr; Found: C, 83.70; H, 10.29. $C_{18}H_{26}O$ calc: C, 83.67; H, 10.14%. IR (neat): 3450, 2970, 2930, 2860, 1685, 1445, 1375, 1360, 1264, 1065, 1028, 762, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.46–1.74 (m, 1H, OH), 1.54 (s, 3H, Me), 1.58 (s, 3H, Me), 1.61 (s, 3H, Me), 1.69 (s, 3H, Me), 1.99–2.12 (m, 4H, CH_2), 2.55 (d, J 8 Hz, 2H, CH_2), 4.94–5.08 (m, 2H, olefin H), 7.22–7.52 (m, 5H, Ph); MS: m/z (rel. intensity) 240 ($M^+ - H_2O$, 1), 138 (19), 121 (100), 95 (19), 69 (15), 43 (18).

3,7-Dimethyl-2-phenyl-3-vinyl-6-octen-2-ol. B.p. 150–160 °C/5 Torr; Found: C, 83.49; H, 10.28; $C_{18}H_{26}O$ calc: C, 83.67; H, 10.14%. IR (neat): 3470, 3090, 3060, 2980, 2940, 1678, 1495, 1444, 1412, 1375, 1067, 1030, 1015, 912, 758, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$): 0.95 and 1.03 (each s, 3H, Me), 1.49–1.83 (m, 5H, CH_2 and OH), 1.53, 1.57, 1.60, and 1.65 (each s, 9H, Me), 5.02–5.32 (m, 3H, olefin H), 5.77 and 5.91 (each dd, J 18, 10 Hz, olefin H), 7.25–7.49 (m, 5H, Ph); MS: m/z (rel. intensity) 138 (8), 122 (10), 121 (100), 95 (15), 69 (12), 43 (18).

(E)-2,5-Diphenyl-4-penten-2-ol. B.p. 165 °C/3 Torr; Found: C, 85.84; H, 7.65. $C_{17}H_{18}O$ calc: C, 85.68; H, 7.61%. IR (neat): 3570, 3450, 3090, 3075, 3040, 2985, 2940, 1600, 1496, 1447, 1375, 1070, 1030, 972, 953, 916, 878, 768, 748, 703, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.60 (s, 3H, Me), 2.04–2.14 (bs, 1H, OH), 2.65 (dd, J 14, 8 Hz, 1H, CH_2), 2.84 (dd, J 14, 7 Hz, 1H, CH_2), 6.04 (ddd, J 16, 8, 7 Hz, 1H, olefin H), 6.50 (d, J 16 Hz, 1H, olefin H), 7.20–7.54 (m, 10H, Ph); MS: m/z (rel. intensity) 220 ($M^+ - H_2O$, 13), 205 ($M^+ - H_2O - Me$, 9), 121 (100), 118 (35), 43 (21).

2,3-Diphenyl-4-penten-2-ol. B.p. 150 °C/3 Torr; Found: C, 85.92; H, 7.73. $C_{17}H_{18}O$ calc: C, 85.68; H, 7.61%. IR (neat): 3570, 3470, 3060, 3040, 2980, 2940, 1602, 1498, 1446, 1375, 1269, 1066, 1027, 1000, 920, 760, 740, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.46 and 1.62 (each s, 3H, Me), 2.02–2.14 (m, 1H, OH), 3.61 and 3.64 (each d, J 10, 8 Hz, 1H, CH), 4.90–5.25 (m, 2H, olefin H), 6.05–6.20 (m, 1H, olefin H), 6.92–7.20 (m, 10H, Ph); MS: m/z (rel. intensity) 220 ($M^+ - H_2O$, 1), 205 ($M^+ - H_2O - Me$, 1), 121 (100), 118 (29), 43 (23).

2-Methyl-2-dodecen-5-ol. B.p. 70 °C/2.5 Torr; Found: C, 78.89; H, 13.49. $C_{13}H_{26}O$ calc: C, 78.72; H, 13.21%. IR (neat): 3360, 2960, 2926, 2875, 2860, 1662, 1450, 1374, 1120, 1080 cm^{-1}; ^{1}H NMR ($CDCl_3$): 0.86–0.93 (m, 3H, Me), 1.22–1.53 (m, 13H, CH_2 and OH), 1.66 (s, 3H, Me), 1.76 (s, 3H, Me), 2.14–2.21 (m, 2H, CH_2), 3.55–3.70 (m, 1H, CH), 5.20 (bt, J 7 Hz, 1H, olefin H); MS: m/z (rel. intensity) 198 (M^+, 1), 197 (6), 71 (6), 70 (100), 69 (15), 55 (11).

3,3-Dimethyl-1-undecen-4-ol. B.p. 74 °C/3 Torr; Found: C, 78.71; H, 13.48. $C_{13}H_{26}O$ calc: C, 78.72; H, 13.21%. IR (neat): 3400, 3080, 2965, 2930, 2860, 1638, 1468, 1460, 1412, 1378, 1117, 1070, 1002, 970, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.22–1.58 (m, 13H, CH_2 and OH), 3.23–3.27 (m, 1H, CH), 5.06 (dd, J 18, 2 Hz, 1H, olefin H), 5.10 (dd, J 11, 2 Hz, 1H, olefin H), 5.83 (dd, J 18, 11 Hz, 1H, olefin H); MS: m/z (rel. intensity) 71 (7), 70 (100), 69 (11), 55 (9).

(E)-11,15-Dimethyl-10,14-hexadecadien-8-ol. B.p. 145 °C/3 Torr; Found: C, 80.86; H, 13.06. $C_{18}H_{34}O$ calc: C, 81.14; H, 12.86%. IR (neat): 3380, 2970, 2930,

2870, 1710, 1452, 1378, 1050, 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$): 0.88 (bt, J 6 Hz, 3H, Me) 1.20–1.53 (m, 13H, CH_2 and OH), 1.61 (s, 3H, Me), 1.64 (s, 3H, Me), 1.69 (s, 3H, Me), 2.02–2.22 (m, 6H, CH_2), 3.54–3.66 (m, 1H, CH), 5.04 (m, 1H, olefin H), 5.18 (t, J 8 Hz, 1H, olefin H); MS: m/z (rel. intensity) 266 (M^+, 2), 248 ($M^+ - H_2O$, 6), 138 (14), 124 (22), 123 (52), 96 (16), 95 (92), 82 (21), 70 (22), 69 (100), 68 (14).

2,6-Dimethyl-6-vinyl-2-tetradecen-7-ol. B.p. 145 °C/3 Torr; Found: C, 81.24; H, 12.97. $C_{18}H_{34}O$ calc: C, 81.14; H, 12.86%. IR (neat): 3480, 3090, 2970, 2930, 2870, 1710, 1623, 1460, 1412, 1378, 1070, 1005, 912 cm^{-1}; ^{1}H NMR ($CDCl_3$): 0.89 (bt, J 6 Hz, 3H, Me), 0.98 and 1.02 (each s, 3H, Me), 1.10–1.57 (m, 15H, CH_2 and OH), 1.60 (s, 3H Me), 1.69 (s, 3H, Me), 1.80–1.98 (m, 2H, CH_2), 3.26–3.34 (m, 1H, CH), 5.01–5.28 (m, 3H, olefin H), 5.68–5.87 (m, 1H, olefin H); MS: m/z (rel. intensity) 248 ($M^+ - H_2O$, 3), 138 (12), 123 (45), 109 (18), 96 (15), 95 (100), 82 (19), 70 (15), 69 (83).

(E)-1-Phenyl-1-undecen-4-ol. B.p. 187 °C/3 Torr; Found: C, 82.64; H, 10.82. $C_{17}H_{26}O$ calc: C, 82.87; H, 10.64%. IR (neat): 3380, 3065, 3030, 2940, 2860, 1598, 1497, 1465, 1448, 1070, 1030, 967, 742, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$): 0.89 (bt, J 6 Hz, 3H, Me), 1.20–1.63 (m, 13H, CH_2 and OH), 2.25–2.55 (m, 2H, CH_2), 3.68–3.83 (m, 1H, CH), 6.26 (dt, J 16, 8 Hz, 1H, olefin H), 6.51 (d, J 16 Hz, 1H, olefin H), 7.21–7.49 (m, 5H, Ph); MS: m/z (rel. intensity) 246 (M^+, 2), 119 (10), 118 (100), 117 (11), 69 (14).

3-Phenyl-1-undecen-4-ol. B.p. 162 °C/3 Torr; Found: C, 82.91; H, 10.94. $C_{17}H_{26}O$ calc: C, 82.87; H, 10.64%. IR (neat): 3470, 3040, 2940, 2870, 1715, 1641, 1603, 1498, 1470, 1455, 1380, 1070, 995, 918, 760, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$): 0.86 (bt, J 7 Hz, 3H, Me), 1.20–1.72 (m, 13H, CH_2 and OH), 3.21–3.38 (m, 1H, CH), 3.77–3.94 (m, 1H, CH), 5.14 (dd, J 16, 2 Hz, 1H, olefin H), 5.24 (dd, J 10, 2 Hz, 1H, olefin H), 5.99–6.25 (m, 1H, olefin H), 7.21–7.46 (m, 5H, Ph); MS: m/z (rel. intensity) 119 (10), 118 (100), 117 (12), 69 (6).

References

1 For recent synthetic studies using allylic phosphates, see, S. Araki and Y. Butsugan, Bull. Chem. Soc. Jpn., 56 (1983) 1446; Y. Okuda, M. Sato, K. Oshima and H. Nozaki, Tetrahedron Lett., 24 (1983) 2015; S. Araki and Y. Butsugan, J. Chem. Soc., Perkin Trans. 1, (1984) 969; S. Araki, S. Manabe and Y. Butsugan, Bull. Chem. Soc. Jpn., 57 (1984) 1433; S. Araki, K. Ohmori and Y. Butsugan, Synthesis, (1984) 841; S. Araki, T. Sato, H. Miyagawa and Y. Butsugan, Bull. Chem. Soc. Jpn., 57 (1984) 3523; Y. Butsugan, A. Yamashita and S. Araki, J. Organomet. Chem., 287 (1985) 103; S.-I. Murahashi and Y. Imada, Chem. Lett., (1985) 1477.

2 For a recent review, see: D.E. Cane, Acc. Chem. Res., 18 (1985) 220, and references cited therein.

3 K. Kimura, K. Takai and H. Nozaki, 45th National Meeting of the Chemical Society of Japan, Tokyo, April 1982, Abstr. No. 3F31.

4 S. Matsubara, K. Wakamatsu, Y. Morizawa, N. Tsuboniwa, K. Oshima and H. Nozaki, Bull. Chem. Soc. Jpn., 58 (1985) 1196.

5 P. Girard, J.L. Namy and H.B. Kagan, J. Am. Chem. Soc., 102 (1980) 2693.

6 F. Barbot and Ph. Miginiac, Tetrahedron Lett., (1975) 3829.

7 F. Gerard and Ph. Miginiac, Bull. Soc. Chim. Fr., (1974) 2527.

8 A. Murai, M. Ono and T. Masamume, Bull. Chem. Soc. Jpn., 50 (1977) 1226.

9 L. Mandall, J. Org. Chem., 22 (1957) 150.

10 M. Mladenova, B. Blagoev, M. Gaudemar, F.G. Bardone and J.Y. Lallemand, Tetrahedron, 37 (1981) 2157.