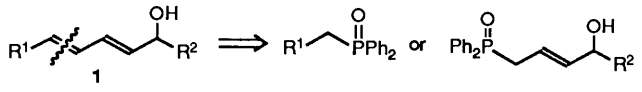
The Synthesis of (*Z*)-Penta-2,4-dien-1-ol and Substituted (*E*)-Pentadienols by the Stereochemically Controlled Horner–Wittig Reaction

Paul S. Brown, Nicholas Greeves, Andrew B. McElroy and Stuart Warren*
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

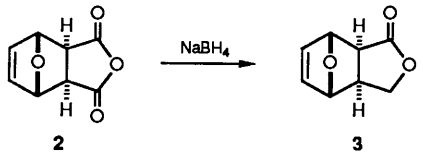
Acylation of $Ph_2P(O)Me$ with a lactone gives a Horner–Wittig intermediate with a *Z*-double bond protected as a Diels–Alder adduct with furan and hence (*Z*)-penta-2,4-dien-1-ol. Substituted (*E*)-penta-2,4-dien-1-ols are available by a more general route involving addition of enals to phosphine oxides, a regiochemically controlled allylic alcohol transposition, and a Horner–Wittig reaction. The geometry of only one double bond can be controlled.

The intramolecular Diels–Alder reaction has been widely used in stereochemically demanding synthesis,[1] as the normal regioselectivity and *endo* stereoselectivity of the intermolecular reaction may be reversed, *e.g.* by linking the diene and dienophile *via* an ester bond.[2] We report[3] that either regiochemistry (Scheme 1) of our phosphine oxide variant[4] of the Horner–Wittig reaction may be used to make pentadienols **1** suitable for ester formation with acrylic acids.[2]



Scheme 1

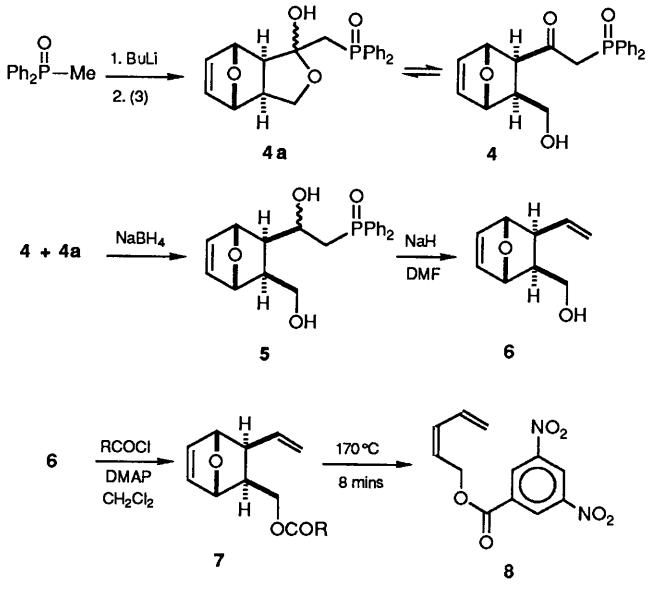
(*E*)-Penta-2,4-dien-1-ol is easily made, but the *Z*-compound has proved elusive. Lindlar reduction of penta-4-en-2-yn-1-ol is reasonably successful, but over-reduction remains a problem,[5] and the Peterson olefination provides an alternative.[6] We report a simple synthesis of the *Z* isomer, conveniently isolated as its 3,5-dinitrobenzoate. We chose to protect the sensitive *Z*-double bond as the Diels–Alder adduct with furan (Scheme



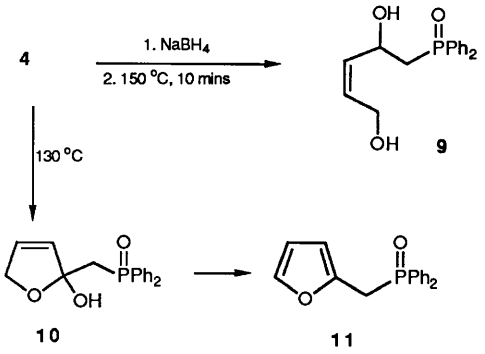
2). Reduction of the *exo*[7] maleic anhydride adduct **2** gave the lactone[8] **3** which cleanly acylated[4,9] the lithium derivative of $Ph_2P(O)Me$ to give the hydroxy ketone **4**: this exists entirely as the hemiacetals **4a**.

Three reactions are still required: reduction of the ketone, the Horner–Wittig elimination, and the retro Diels–Alder reaction and they must be carried out in that order. Reduction of **4** followed by thermolysis cleanly gave the *Z*-diol **9** but the elimination of $Ph_2PO_2^-$ gave no recognisable products. Thermolysis of **4** gave the furan **11** presumably *via* **10**. The correct sequence (Scheme 2) gave the ester **8** in 24% yield from the lactone **3** despite the low yield (42%) in the elimination step. We recommend acylation of **6** with the appropriate acid if a Diels–Alder reaction is intended.

Attempts to extend this approach by adding the lithium derivative of $Ph_2P(O)CH_2R$ to the lactone **3** foundered on the redundant chiral centres. Attempts, summarised in Scheme 3, to deliver the *Z*-alkene as a butenolide **13** made[10] from the lactones **12** or **14** failed because the hydroxy ketone **15** surprisingly emerged with an *E*-double bond and even more surprisingly gave the furan **16** with time. Oxidation of such furans (Scheme 4) did give a *Z*-dienone **21** but this was very unstable and we could not reduce either carbonyl group without



Scheme 2



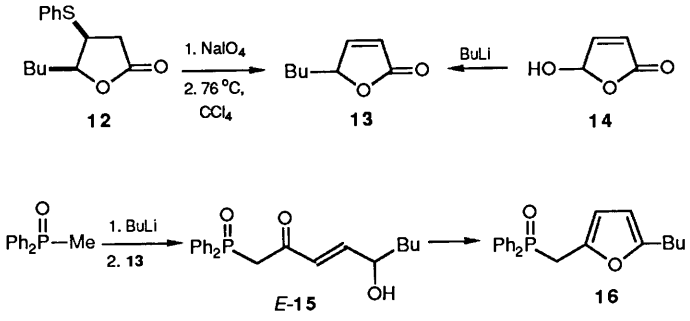
also reducing the alkene or transforming *Z*-**21** into *E*-**21** (Table 1).

A more general approach[3] (Scheme 5) developed from the Horner–Wittig reaction of the unsaturated hydroxyalkylphosphine oxides **25** made by allylic rearrangement under Babler's conditions.[11] Addition of the lithium derivatives of alkyl diphenylphosphine oxides to conjugated enones or enals occurred exclusively in the 1,2 sense. Rearrangement (Ac_2O, AcOH, TsOH)[11] gave the allylically transposed esters **24** except when $R^1 = R^2 = R^3 = H$. Such rearrangements usually rely on the stability of the intermediate allylic cation **27** for favourable kinetics and on a more highly substituted double bond in the product **24** than in the alternative ester **26** for favourable thermodynamics.[12] The failure of **23a** to rearrange

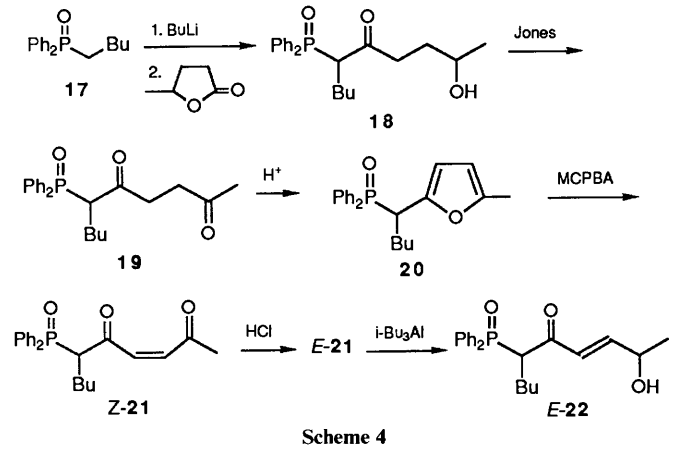
Table 1 Reduction of the enedione **21**

Reagent	Solvent	Stoichiometry[a]	Temp. (°C)	Result[b] (yield, %)
Reductions of *Z*-**21**				
$NaBH_4$	MeOH	3	−78 to 0	A
$Zn(BH_4)_2$	Et_2O	3	0 to room temp.	A
$NaBH_3/Ce^{3+}$	MeOH	2.0	0	A
L-Selectride[c]	THF	1.0	−78	A
	THF	3.0	−78 to 0	B
$LiAlH(OBu^t)_3$	THF	6.0	−78 to room temp.	A
	THF	6.0	0	B
9-BBN[d]	THF	2.1	0 to 25	C
	THF	1.05	−10 to 25	C (38)
	THF	1.0	−78 to 10	A
DIBAL[e]	Toluene	3.0	−10	A
	Toluene	2.2	−10	E (35)
	Toluene	2.0	0	E (20)
	Toluene	1.5	−78 to room temp.	E (35)
DIBAC[f]	Toluene	13	−78 to 0	A
Reductions of *E*-**21**				
$NaBH_4/Ce^{3+}$	MeOH	2.1	Room temp.	A
$Zn(BH_4)_2$	Et_2O	20	0 to room temp.	A
DIBAL[c]	Toluene	3	0	E
	Toluene	1	−5	B, F[h]
Red-Al[g]	Toluene	1	0	B, D, F[h]
$LiAlH_4$	Et_2O	1.9	0	D (28)
	Et_2O	1.0	−5	B[h] (22)
$AlBu^i_3$	Et_2O	2	Room temp.	D (29)

[a] Ratio of molar equivalents of reducing agent to **21**. [b] Results: A = no olefinic protons in NMR spectrum, double bond presumably reduced; B = furan **20**; C = diketone **19**; D = allylic alcohol **22**; E = some olefinic protons in NMR spectrum, but no identified product; F = *E*-enedione *E*-**21**. [c] Lithium tri-*sec*-butylborohydride. [d] 9-Borabicyclo[3.3.1]nonane. [e] Diisobutylaluminium hydride. [f] Diisobutylaluminium-2,6-di-*tert*-butyl-4-methylphenoxide. [g] Sodium bis(2-methoxyethoxy)aluminium hydride. [h] Dilute HCl work-up.

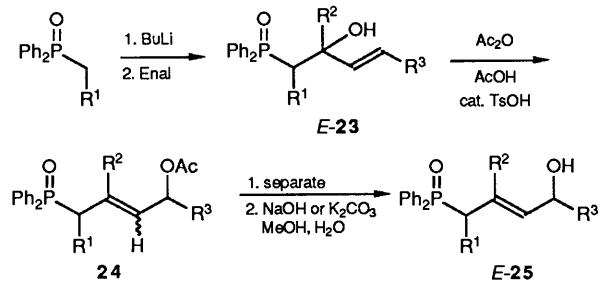


Scheme 3



Scheme 4

(Table 2) and the success of **23d, f** fit these expectations, but the successful rearrangements of **23b** and **23e** are surprising as the double bond in the starting material **23** or **26** and in the product **24** is equally substituted. The only difference is that the acetate moves away from the Ph_2PO group. We take this to be a steric effect, though there could be an electronic contribution as both AcO and Ph_2PO are electron-withdrawing.



Scheme 5

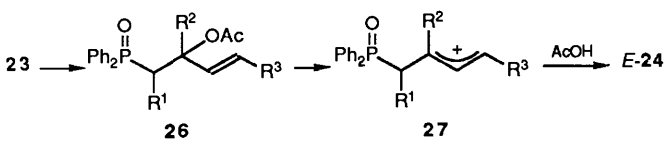
Though the number of substituents does not affect the position of the double bond in the product **24**, it does affect its geometry (Table 2). If $R^1 \neq H$, only *E*-**24** is formed **24e, f**. If $R^2 = H$, only *E*-**24** is formed whether $R^1 = H$ or alkyl. Again we assume these are simple steric effects. If R^2 = alkyl, the product **24** is formed as a 1:1 *E*:*Z* mixture **24c, d**. These geometrical isomers were easily separated by chromatography and the products hydrolysed to the alcohols **25** in high yield over the two steps (Table 2). There is, however, no control over tetrahedral stereochemistry during this rearrangement. Either diastereoisomer of the alcohol, (**23**; $R^1 \neq H$, $R^3 \neq H$) rearranged to the same mixture of diastereoisomers of the products **24** as expected for a mechanism involving an allylic cation **27**. We have an alternative method[13] for such rearrangements which is nearly stereospecific.

Other rearrangement methods were less successful. Treat-

Table 2 Rearrangement of the allylic alcohols **23** (Scheme 5)

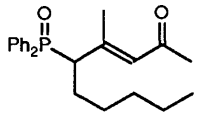
	Starting material					Products				
	Yield (%)	R^1	R^2	R^3	Method[a]		Yield (%)	Stereo		Yield (%)
23a	85	H	H	H	A	**26a**	—	*E*	—	—
23b	88	H	H	Me	A	**24b**	83	*E*	**25b**	86
23c	80	H	Me	H	A	*E*-**24c**	47		*E*-**25c**	76
						Z-**24c**	46		*Z*-**25c**	62
23d	84	H	Me	Me	A	*E*-**24d**	45		*E*-**25d**	90
						Z-**24d**	46		*Z*-**25d**	80
23e	98	n-C_5H_{11}	H	Me	A	**24e**	98	*E*[b]	*E*-**25e**	—[c]
23f	65	n-C_5H_{11}	Me	Me	A	**24f**	77	*E*[b]	*E*-**25f**	—[c]
					B	**25f**	16	*E*		
					C	**28**	60	*E*		

[a] Method A = Ac_2O, AcOH, cat. TsOH, 0 °C, 15 min (R^2 = H) or room temperature, 24 h (R^2 = H); Method B = dilute HCl in dioxane, see. ref. 18; Method C = PCC in dichloromethane, see ref. 14. [b] As a mixture of diastereoisomers. [c] The elucidation of structure and synthesis and characterisation of individual diastereoisomers of **25e** and **25f** was achieved by a different method, see ref. 13.



26 **27**

ment of **23f** with acid gave a low yield of **25f**, the main side reaction being elimination. Oxidation of **23f** with PCC[14] gave the rearranged ketone **28** in better yield and this could be reduced to **25f** with sodium borohydride.



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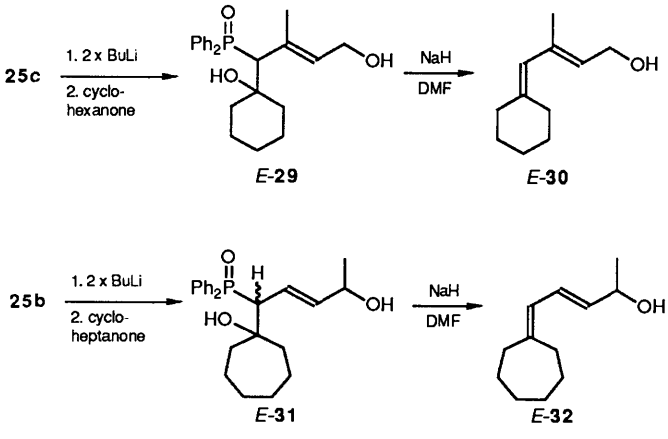
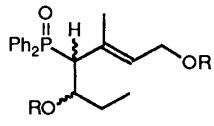
Horner–Wittig Reactions.—We have used dilithium derivatives of hydroxyalkylphosphine oxides in the synthesis of unsaturated alcohols.[9] The unsubstituted compound *E*-**25** (R^1 = R^2 = R^3 = H) has been used in one-step Horner–Wittig reactions.[15] It quickly became clear that, while the dilithium derivatives of the *Z*-alcohols **25** would not add to aldehydes or ketones, those from the *E*-alcohols **25** added successfully. We made two simple diene alcohols *E*-**30** and *E*-**32** from symmetrical ketones to illustrate the method (Scheme 6). The adduct **31** is a mixture of diastereoisomers but gives a single alkene on elimination. In both cases the *E*-geometry of the starting material is retained in the products.



Scheme 6



33

Attempts to control the stereochemistry of the double bond formed in the Horner–Wittig reaction were thwarted by our inability to separate the diastereoisomers of **33** (R = H, Ac or $SiMe_3$) even by HPLC. We have since developed alternative chemistry from intermediates **24** to give double bonds with controlled stereochemistry.[13,16]

Experimental

5-exo-(2′-*Diphenylphosphinoyl*-1′-*oxoethyl*)-6-exo-*hydroxymethyl*-7-*oxabicyclo*[2.2.1]*hept*-2-*ene Hemiacetal* **4a**.—Butyllithium (1.5 mol dm^{-3} solution in hexane; 6.7 ml) was added to a stirred solution of methyldiphenylphosphine oxide (2.16 g, 10 mmol) in dry THF (50 ml) under nitrogen at 0 °C. After 20 min, the yellow solution was cooled to −78 °C and the lactone[8] **3** (1.52 g, 10 mmol) in dry THF (10 ml) was added dropwise. Saturated aqueous ammonium chloride (30 ml) was added at −78 °C. The reaction mixture was allowed to warm to room temperature and the THF evaporated under reduced pressure. The aqueous residues were extracted with dichloromethane (3 × 30 ml) and the combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Flash chromatography[19] on silica eluting with EtOAc–MeOH (49:1) and recrystallisation from EtOAc–CH_2Cl_2 gave the *hemiacetal* (2.2 g, 60% or 85% based on consumed starting material) as prisms, m.p. 136–138 °C (Found: C, 68.6; H, 5.65; P, 8.5. $C_{21}H_{21}O_4P$ requires C, 68.7; H, 5.75; P, 8.4%); R_F 0.2; ν_{max}/cm^{-1} 3330 (OH), 1610 (C=C), 1450 (PhP) and 1180 (P=O); ^1H NMR spectrum too complex to interpret but shows signals in the expected regions; *m*/*z* 282 (8%, M − C_4H_4O − H_2O), 281 (9, M − $C_4H_7O_2$), 216 (5, Ph_2POMe), 215 (20, Ph_2POCH_2), 202 (20, Ph_2POH), 201 (100, Ph_2PO) and 68 (100, C_4H_4O).

5-exo-(2′-*Diphenylphosphinoyl*-1′-*hydroxyethyl*)-6-exo-*hydroxymethyl*-7-*oxabicyclo*[2.2.1]*hept*-2-*ene* **5**.—Sodium borohydride (60 mg) was added in small portions over 1.5 h to a stirred solution of the hemiacetal **4a** (104 mg) in methanol (10 ml) at 0 °C. Saturated aqueous ammonium chloride (5 ml) was added and the methanol was removed under reduced pressure. The aqueous residue was acidified with dilute HCl, diluted with brine (5 ml) and extracted with dichloromethane

(3 × 20 ml). The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Preparative TLC on silica eluting twice with CH_2Cl_2–MeOH (19:1) gave the higher running *diol* (36 mg, 34%) as a gum, R_F(CH_2Cl_2–MeOH 9:1) 0.34; ν_{max}/cm^{-1} 3350 (OH), 1590 (C=C), 1440 (P–Ph) and 1150 (P=O); δ_H 8.0–7.4 (10 H, m, Ph_2PO), 6.4 (1 H, dd, *J** 6 and 2, C=CH), 6.15 (1 H, dd, *J* 6 and 2, HC=C), 4.6 (2 H, br d, *J* 2, HCOCH), 4.3 (1 H, m, C*H*OH), 4.6–3.6 (2 H, br m, exchanges with D_2O, 2 × OH), 3.75 (2 H, m, CH_2OH), 2.7 (2 H, m, CH_2P) and 1.9 (2 H, m, remaining CHs) (Found: M^+ – H, 369.1279. $C_{21}H_{22}O_4P$ requires M, 369.1256); *m/z* 369 (0.19%, M – H), 322 (22, M – C_4H_4O), 245 (28, Ph_2POCH_2CHOH), 216 (45, Ph_2POMe), 215 (82, Ph_2POCH_2), 202 (90, Ph_2POH) and 201 (100, Ph_2PO), and the lower running *diol* (64 mg, 61%) as a gum, R_F(CH_2Cl_2–MeOH 9:1) 0.28; ν_{max}/cm^{-1} 3370 (OH), 1595 (C=C), 1440 (PhP) and 1160 (P=O); δ_H 8.0–7.4 (10 H, m, Ph_2PO), 6.3 (2 H, br s, HC=CH), 5.1 (1 H, br s, *H*COCH), 4.85 (1 H, br s, HCOC*H*), 4.35 (1 H, m, C*H*OH), 5.1–3.5 (2 H, br m, exchanges with D_2O, 2 × OH), 3.7 (2 H, m, CH_2OH), 2.7 (2 H, dd, J_{HP}11, J_{HH} 6, CH_2P) and 1.8 (2 H, br ABq, remaining CHs) (Found: M^+ – H, 369.1266. $C_{21}H_{22}O_4P$ requires M, 369.1256); *m/z* 369 (0.91%, M – H), 322 (2.9, M – C_4H_4O), 245 (25, Ph_2POCH_2CHOH), 216 (55, Ph_2POMe), 215 (94, Ph_2POCH_2), 202 (97, Ph_2POH) and 201 (100, Ph_2PO).

6-exo-*Hydroxymethyl*-5-exo-*vinyl*-7-*oxabicyclo*[2.2.1]*hept*-2-*ene* **6**.—Sodium hydride (50% dispersion in oil; 36 mg) was added to a stirred solution of the diols **5** (138 mg) in dry DMF (5 ml). The solution was warmed to 50 °C for 3 h 20 min and was stirred for 16 h at room temperature. Work-up followed by flash chromatography eluting with EtOAc gave the *alkene* (24 mg, 42%) as an oil, R_F 0.39; ν_{max}/cm^{-1} 3500 and 3300 (OH) and 1600 (C=C); δ_H 6.37 (2 H, m, 2-H and 3-H), 5.85 (1 H, dt, *J* 17 and 9.4, 1′-H), 5.16 (1 H, dd, *J* 9.4 and 2.6, 2′-H_A), 5.14 (1 H, dd, *J* 17 and 2.6, 2′-H_B), 4.88 (1 H, br s, 1-H), 4.64 (1 H, br s, 4-H), 3.75 (1 H, dd, *J* 10.5 and 6.5, 1″-H_A), 3.53 (1 H, dd, *J* 10.5 and 8, 1″-H_B), 2.36 (1 H, dd, *J* 8 and 9.4, 5-H) and 1.9 (1 H, dt, *J* 6.5 and 8, 6-H) (Found: M^+ – C_4H_4O, 84.0577. C_5H_8O requires M, 84.0575); *m/z* 84 (60%, M – C_4H_4O) and 68 (100, C_4H_4O).

6-exo-(3,5-*Dinitrobenzoyloxymethyl*)-5-exo-*vinyl*-7-*oxabicyclo*[2.2.1]*hept*-2-*ene* **7**.—3,5-Dinitrobenzoyl chloride (30 mg), the alcohol **6** (15 mg) and DMAP (30 mg) in CH_2Cl_2 (2 ml) for 5 min gave, after flash chromatography on silica gel eluting with Et_2O–light petroleum (b.p. 40–60 °C), the *ester* (23 mg, 67%) as needles, m.p. 97–98 °C; R_F(Et_2O) 0.79; ν_{max}/cm^{-1} 1730 (C=O), 1630 (C=C), 1550 (NO_2) and 1350 (NO_2); δ_H 9.23 (1 H, t, *J* 2, *p*-ArCH), 9.15 (2 H, d, *J* 2, *o*-ArCH), 6.44 (2 H, s, HC=CH), 5.80 (1 H, dt, *J* 17 and 10, 1′-H), 5.26–5.17 (2 H, m, 2′-H's), 4.91 (1 H, s, 1-H), 4.73 (1 H, s, 4-H), 4.52 (1 H, dd, *J* 5.8 and 11, 1″-H_A), 4.34 (1 H, dd, *J* 9.7 and 11, 1″-H_B), 2.49 (1 H, dd, *J* 8.2 and 10, 5-H) and 2.20 (1 H, ddd, *J* 8.2, 5.8 and 9.7, 6-H) (Found: M^+ – C_4H_4O, 278.0560. $C_{12}H_{10}N_2O_6$ requires M, 278.0539); *m/z* 278 (3%, M – C_4H_4O), 195 (28, $C_7H_3N_2O_5$) and 68 (100, C_4H_4O).

(Z)-1-(3,5-*Dinitrobenzoyloxy*)*penta*-2,4-*diene* **8**.—The ester **7** (2.52 mg) was distilled in a Kugelrohr apparatus at 170 °C and 0.2 mmHg for 8 min to give the diene (1.82 mg, 90%) as a pale yellow solid, m.p. 60–64 °C (lit.,[5] m.p. 62–66 °C).

(Z)-5-*Diphenylphosphinoyl*-4-*hydroxypent*-2-*en*-1-*ol* **9**.—The hemiacetal **4a** (223 mg) was reduced as above to a mixture of diols. The mixture was heated in a rotating Kugelrohr apparatus for 10 min at 150 °C and 0.85 mmHg. Flash chromatography of the residue on silica eluting with CH_2Cl_2–MeOH (9:1) gave the *diol* (151 mg, 83%) as an oil (Found: C, 67.3; H, 6.55; P, 10.2. $C_{17}H_{19}O_3P$ requires C, 67.5; H, 6.35; P, 10.2%); R_F(CH_2Cl_2–MeOH, 9:1) 0.55; ν_{max}/cm^{-1} 3590 (OH), 3340 (OH), 1590 (C=C), 1435 (PhP), 1150 (P=O) and 915 (C–O); δ_H 7.7–7.25 (10 H, m, Ph_2PO), 5.53 (1 H, dt, *J* 11 and 6.6, C*H*CH_2OH), 5.39 (1 H, dd, *J* 11 and 8, C*H*CHOH), 4.97 (1 H, m, C*H*OH), 4.00 (1 H, m, exchanges with D_2O, OH), 3.95 (2 H, d, *J* 6.6, CH_2OH), 2.63 (1 H, ddd, J_{AB} 15, J_{AX} 7.6, J_{AP} 10.8, CH_AH_BP) and 2.40 (1 H, ddd, J_{AB} 15, J_{BX} 5.5, J_{BP} 9, CH_AH_BP) (Found: M^+ – H_2O, 284.0962. $C_{17}H_{17}O_2P$ requires M – H_2O, 284.0966); *m/z* 284 (14%, M – H_2O), 216 (60, Ph_2POMe), 215 (90, Ph_2POCH_2), 202 (70 , Ph_2POH) and 201 (100, Ph_2PO).

2-*Diphenylphosphinoylmethylfuran* **11**.—The hemiacetal **4** (206 mg) was heated in a Kugelrohr apparatus to 130 °C at 0.75 mmHg. A violent reaction ensued evolving furan. Flash chromatography of the residue on silica eluting with EtOAc gave the *furan* (126 mg, 99.6%) as needles, m.p. 126–127 °C (from EtOAc); R_F 0.30; ν_{max}/cm^{-1} 2980 (CH), 1590 (C=C), 1440 (Ph–P) and 1170 (P=O); δ_H 8.0–7.4 (10 H, m, Ph_2PO), 7.3 (1 H, m, CHO), 6.3 (1 H, m, C*H*=CHO), 6.1 (1 H, m, CHCO) and 3.8 (2 H, d, J_{HP} 14, CH_2P) (Found: M^+, 282.0809. $C_{17}H_{15}O_2P$ requires M, 282.0809); *m/z* 282 (5.7%, M^+), 216 (18, Ph_2POMe), 215 (35, Ph_2POCH_2), 202 (15, Ph_2POH) and 201 (100, Ph_2PO).

5-*Butylfuran*-2(5*H*)-*one* **13**.—Sodium periodate (400 mg) dissolved in water (2 ml) was added to a stirred solution of the lactone[10] **12** (445 mg) in methanol (5 ml) at 0 °C and the mixture was stirred for 3 days. Aqueous sodium thiosulphate was then added. The aqueous reaction mixture was extracted with chloroform (3 × 10 ml) and the combined organic extracts were dried ($MgSO_4$), and evaporated under reduced pressure. The residue was dissolved in carbon tetrachloride and heated to 76 °C in an NMR tube until reaction was complete. Distillation of the residue (Kugelrohr apparatus) gave the butenolide (150 mg, 60%) as a clear oil (b.p. 55–60 °C/0.6 mmHg), R_F(CH_2Cl_2) 0.29, with spectroscopic data as previously reported.[8]

(E)-1-*Diphenylphosphinoyl*-5-*hydroxynon*-3-*en*-2-*one* **15**.—Butyl-lithium (1.5 mol dm^{-3} solution in hexane; 0.25 ml) was added to a stirred solution of methyldiphenylphosphine oxide (80 mg) in dry THF (10 ml) under nitrogen at 0 °C. After 15 min, the yellow solution was cooled to −78 °C and the butenolide **13** (30 mg) in dry THF (5 ml) was added dropwise. The temperature was maintained at −78 °C for 2 h when saturated aqueous ammonium chloride (10 ml) was added. The THF was removed under reduced pressure. The aqueous residues were extracted with dichloromethane (3 × 20 ml) and the combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Preparative TLC of the residue on silica eluting with EtOAc gave two main products and recovered phosphine oxide. The higher running product, 2-*butyl*-5-*diphenylphosphinoylmethylfuran* **16** (13 mg, 18%) was a gum, δ_H 7.9–7.3 (10 H, m, Ph_2PO), 5.95 (1 H, d, *J* 3, =C*H*CH=), 5.8 (1 H, d, *J* 3, =CHC*H*=), 3.7 (2 H, d, J_{HP} 14, CH_2P), 2.4 (2 H, t, *J* 7, CH_2CO), 1.4–1.0 (4 H, m, CH_2CH_2) and 0.85 (3 H, t, *J* 6, Me); *m/z* 338 (5%, M^+), 216 (5, Ph_2POMe), 215 (30, Ph_2POCH_2), 202 (30, Ph_2POH), 201 (100, Ph_2PO) and 137 (100, M – Ph_2PO). The lower running product, 1-*diphenylphosphinoyl*-5-*hydroxynon*-3-*en*-2-*one* **15** (13 mg, 17%) was a gum, ν_{max}/cm^{-1} 3340 (OH), 1685 (C=O), 1630 (C=C), 1437 (PhP), 1170 (P=O) and 915 (CH def.); δ_H 7.8–7.4 (10 H, m, Ph_2PO), 6.9 (1 H, dd, *J* 4 and 14, *H*C=CHCO), 6.5 (1 H, d, *J* 14, HC=C*H*CO), 4.25 (1 H,

* Throughout *J* values are given in Hz.

dt, *J* 4 and 6, C*H*OH), 3.7 (2 H, d, J_{HP} 13, CH_2P), 1.7–1.1 [6 H, m, $(CH_2)_3$] and 0.85 (3 H, t, *J* 7, Me); *m/z* 356 (5%, M^+), 338 (100, M − H_2O), 299 (20, M − C_4H_9), 298 (60, M − C_4H_{10}), 216 (15, Ph_2POMe), 215 (30, Ph_2POCH_2), 202 (40, Ph_2POH), 201 (100, Ph_2PO) and 137 (100, M − H_2O − Ph_2PO).

6-*Diphenylphosphinoyldecane*-2,5-*dione* **19**.—Jones reagent was added dropwise to a stirred solution of the keto alcohol[4,9] **18** (1.05 g, 2.82 mmol) in acetone (50 ml) at 0 °C until a permanent orange coloration was obtained. The solution was stirred for 45 min, and then poured carefully into saturated sodium hydrogen carbonate solution (75 ml) and extracted with Et_2O (2 × 75 ml). The combined extracts were washed with aqueous sodium hydrogen carbonate (2 × 50 ml) and water (2 × 50 ml), dried ($MgSO_4$) and evaporated under reduced pressure to give the *diketone* (974 mg, 93%) as needles (from EtOAc–hexane), m.p. 125–126 °C (Found: C, 71.1; H, 7.60; P, 8.4. $C_{22}H_{27}O_3P$ requires C, 71.3; H, 7.35; P, 8.4%), R_F 0.26; ν_{max}/cm^{-1} 1700 (C=O), 1440 (PhP) and 1160 (P=O); δ_H 8.1–7.4 (10 H, m, Ph_2PO), 3.75 (1 H, dt, *J* 3 and 11, CHP), 2.9–2.4 (4 H, m, $COCH_2CH_2CO$), 2.15 (3 H, s, MeCO), 2.0–1.0 (6 H, m, remaining CH_2's) and 0.8 (3 H, m, $MeCH_2$) (Found: M − MeCO, 327.1527. $C_{20}H_{24}O_2P$ requires M, 327.1514); *m/z* 327 (20%, M − MeCO), 243 [23, $Ph_2PO(CH_2)_3$], 229 [53, $Ph_2PO(CH_2)_2$] and 201 (100, Ph_2PO).

2-(1-*Diphenylphosphinoylpentyl*)-5-*methylfuran* **20**.—The above diketone (2.03 g, 5.49 mmol) and Amberlyst 15 resin (100 mg) in dry toluene (50 ml) were refluxed with azeotropic removal of water for 24 h. The mixture was cooled and the toluene was evaporated under reduced pressure. The solid residue was dissolved in CH_2Cl_2 and the resin was removed by filtration. The CH_2Cl_2 was evaporated under reduced pressure to give the *furan* (1.85 g, 96%) as needles, m.p. 135–145 °C (Found: C, 74.5; H, 7.00; P, 8.8. $C_{22}H_{25}O_2P$ requires C, 75.0; H, 7.15; P, 8.8%); R_F 0.38; ν_{max}/cm^{-1} 1600 (C=C and 1440 (PhP); δ_H 7.9–7.2 (10 H, m, Ph_2PO), 5.99 (1 H, t, *J* 3, =C*H*CH=), 5.80 (1 H, dd, *J* 3 and 1, =CHC*H*=), 3.62 (1 H, dt, J_{PH} 12.5, J_t 7.7, CHP), 2.08 (3 H, br s, MeCO), 1.9 (2 H, m, CH_2CP), 1.5–1.1 [4 H, m, $(CH_2)_2$] and 0.79 (3 H, t, *J* 6, $MeCH_2$) (Found: M^+, 352.1618. $C_{22}H_{25}O_2P$ requires M, 352.1592); *m/z* 352 (10%, M^+), 201 (23, Ph_2PO) and 151 (100, M − Ph_2PO).

(Z)-6-*Diphenylphosphinoyldec*-3-*ene*-2,5-*dione* Z-**21**.—MCPBA (50% dispersion; 275 mg, 0.80 mmol) was added to a stirred solution of the furan **20** (255 mg, 0.72 mmol) in dry CH_2Cl_2 (5 ml) at −5 °C. The mixture was stirred for 16 h, diluted with CH_2Cl_2 (50 ml), washed with 10% aqueous sodium sulphite (30 ml), aqueous sodium hydrogen carbonate (3 × 30 ml) and brine (30 ml), dried ($MgSO_4$) and evaporated under reduced pressure without heating to give the unstable *enedione* (260 mg, 98%) as needles, R_F 0.27; ν_{max}/cm^{-1} 1700br (C=O), 1600 (C=C), 1575 (Ph), 1440 (PhP) and 1160 (P=O); δ_H 8.1–7.3 (10 H, m, Ph_2PO), 6.55 (1 H, d, *J* 12, *H*C=CH), 6.2 (1 H, d, *J* 12, HC=C*H*), 3.7 (1 H, m, CHP), 2.3–1.0 (8 H, m, remaining CH_2's), 1.95 (3 H, s, MeCO) and 0.7 (3 H, m, $MeCH_2$); *m/z* 368 (9%, M^+), 325 (24, M − MeCO), 299 [21, M − $MeCO(CH)_2$], 229 [39, $Ph_2PO(CH_2)_2$], 219 (36, $Ph_2PO_2H_2$) and 201 (100, Ph_2PO).

(E)-6-*Diphenylphosphinoyldec*-3-*ene*-2,5-*dione* E-**21**.—MCPBA (50% dispersion; 1.04 g, 3.0 mmol) was added to a stirred solution of the furan **20** (0.97 g, 2.8 mmol) in dry CH_2Cl_2 (20 ml) at −5 °C. The mixture was stirred for 16 h and 10 drops of concentrated HCl were added. After 20 min, the dichloromethane was evaporated under reduced pressure. The residue was purified by flash chromatography (18 × 6) eluting with EtOAc–hexane (3:1) to give the *enedione* (900 mg, 89%) as yellow needles (from EtOAc–hexane), m.p. 143–145 °C (Found: C, 71.5; H, 6.80; P, 8.4. $C_{22}H_{25}O_3P$ requires C, 71.7; H, 6.85; P, 8.4%); R_F 0.43; ν_{max}/cm^{-1} 1680 (C=O), 1600 (C=C), 1440 (Ph–P) and 1175 (P=O); δ_H 8.1–7.3 (10 H, m, Ph_2PO), 7.1 (1 H, d, *J* 16, *H*C=CH), 6.65 (1 H, d, *J* 16, HC=C*H*), 3.83 (1 H, ddd, *J* 3, 11, 13, CHP), 2.2 (3 H, s, MeCO), 1.4–1.0 [6 H, m, $(CH_2)_3$] and 0.84 (3 H, t, *J* 6, $MeCH_2$) (Found: M^+, 368.1522. $C_{22}H_{25}O_3P$ requires M, 368.1541); *m/z* 368 (2%, M^+), 325 (37, M − MeCO), 229 [30, $Ph_2PO(CH_2)_2$], 219 (40, $Ph_2PO_2H_2$), 201 (90, Ph_2PO) and 169 (100).

(E)-6-*Diphenylphosphinoyl*-5-*oxodec*-3-*en*-2-*ol* E-**22**.—Triisobutylaluminium (1 mol dm^{-3} solution in hexane; 0.76 ml, 0.76 mmol) was added to a stirred solution of the enedione *E*-**21** (139 mg, 0.38 mmol) in dry Et_2O (20 ml) at room temperature. The solution was stirred for 19 h and saturated aqueous ammonium chloride (20 ml) was added. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 25 ml). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with EtOAc to give the *alcohol* (41 mg, 29%) as a gum, R_F 0.35; ν_{max}/cm^{-1} 3330 (OH), 1690 (C=O), 1620 (C=C), 1440 (PhP) and 1120 (C–O); δ_H 8.1–7.3 (10 H, m, Ph_2PO), 6.9 (1 H, dd, *J* 18 and 3, =C*H*CHOH), 6.6 (1 H, d, *J* 18, =CHC=O), 4.9 (1 H, m, OH), 4.4 (1 H, m, CHO), 3.7 (1 H, m, CHP), 2.0–0.9 [6 H, m, $(CH_2)_3$], 1.2 (3 H, d, *J* 7, MeCO) and 0.8 (3 H, m, $MeCH_2$) (Found: MH^+, 371.1742. $C_{22}H_{28}O_3P$ requires M, 371.1776); *m/z* 371 (1%, MH^+), 355 (2, M − Me), 352 (1, M − H_2O), 325 (20, M − MeCHOH), 229 [70, $Ph_2PO(CH_2)_2$], 219 (45, $Ph_2PO_2H_2$) and 201 (100, Ph_2PO).

1-*Diphenylphosphinoylbut*-3-*en*-2-*ol* **23a**.—Butyl-lithium (1.6 mol dm^{-3} in hexane; 20 ml) was added dropwise to a stirred solution of methyldiphenylphosphine oxide (6.5 g) in dry THF (250 ml) under nitrogen at −78 °C. After 20 min, a solution of acrolein (commercial 90%; 2 ml) in dry THF (2 ml) was added. Aqueous ammonium chloride (50 ml) and aqueous sodium metabisulphite (30 ml) were added at room temperature. The layers were separated, and the aqueous layer was extracted with ethyl acetate (2 × 50 ml). The combined organic extracts were washed with aqueous sodium metabisulphite (2 × 100 ml), water (50 ml) and brine (2 × 50 ml), dried ($Na_2SO_4/MgSO_4$) and evaporated under reduced pressure. Column chromatography of the residue on silica, eluting with ethyl acetate, gave the *alcohol* (6.95 g, 85%) as an oil, R_F (EtOAc) 0.20; $\nu_{max}(CHCl_3)/cm^{-1}$ 3350 (OH), 1640 (C=C), 1440 (PPh) and 1260 (P=O); $\delta_H(CDCl_3)$ 8.0–7.0 (10 H, m, Ph_2PO), 5.0–5.55 [1 H, ddd, *J* 12, 9 and 5, CH(OH)C*H*=CH_2], 5.3 (1 H, d, *J* 9, CH=CH_AH_B), 4.95 (1 H, d, *J* 12, CH=CH_AH_B), 5.4–4.4 (2 H, m, C*H*OH and OH) and 2.9–2.5 (2 H, m, Ph_2PCH_2). This alcohol was characterised as its acetate **26a** below.

(E)-1-*Diphenylphosphinoylpent*-3-*en*-2-*ol* **23b**.—In the same way, butyl-lithium (1.6 mol dm^{-3} solution in hexane; 6.7 ml), methyldiphenylphosphine oxide (2.16 g), and crotonaldehyde (710 mg) gave the *alcohol* (2.50 g, 88%) as prisms, m.p. 102–103 °C (from EtOAc) (Found: C, 71.7; H, 6.6; P, 10.6. $C_{17}H_{19}PO_2$ requires C, 71.3; H, 6.7; P, 10.8%); R_F (EtOAc–ethanol, 6:1) 0.45; $\nu_{max}(CHCl_3)/cm^{-1}$ 3350 (OH), 1660 (C=C), 1430 (PPh) and 1300 (P=O); $\delta_H(CDCl_3)$ 8.0–7.4 (10 H, m, Ph_2PO), 5.9–5.3 (2 H, m, HC=CH), 4.6 (2 H, m, OH and C*H*OH), 2.9–2.3 (2 H, m, PCH_2) and 1.55 (3 H, d, *J* 7, CHMe); *m/z* 286 (4%, M^+), 268 (10, M − H_2O) and 216 [65, $Ph_2P(OH)CH_2$].

1-*Diphenylphosphinoyl*-2-*methylbut*-3-*en*-2-*ol* **23c**.—In the same way, butyllithium (1.6 mol dm^{-3} in hexane; 12.5 ml), methyldiphenylphosphine oxide (4.32 g), and butenone (1.6 g)

gave the *alcohol* (4.53 g; 79%) as needles, m.p. 98–99 °C (from EtOAc) (Found: C, 71.2; H, 6.7; P, 10.8. $C_{17}H_{19}PO_2$ requires C, 71.3; H, 6.7; P, 10.8%); R_F (EtOAc) 0.46; $\nu_{max}(CDCl_3)/cm^{-1}$ 3370 (OH), 1440 (PPh) and 1180 (P=O); $\delta(CDCl_3/D_2O)$ 8.0–7.3 (10 H, m, Ph_2PO), 5.8 (1 H, dd, *J* 17 and 11, $CH_A{=}CH_BH_C$), 5.3 (1 H, dd, *J* 17 and 2, $CH_A{=}CH_BH_C$), 4.85 (1 H, dd, *J* 11 and 2, $CH_A{=}CH_BH_C$), 2.7 (2 H, d, J_{HP} 11, PCH_2) and 1.35 (3 H, s, Me); *m/z* 286 (5%, M^+), 285 (5, M − H), 271 (20, M − Me), 216 [50, $Ph_2P(OH)CH_2$], 215 [100, $Ph_2P(O)CH_2$], 202 (20, Ph_2POH) and 201 (70, Ph_2PO).

1-*Diphenylphosphinoyl*-2-*methylpent*-3-*en*-2-*ol* E-**23d**.—In the same way, butyllithium (1.6 mol dm^{-3} in hexane; 13.1 ml), methyldiphenylphosphine oxide (4.32 g) and pent-3-en-2-one (1.85 g) gave the *alcohol* (5.02 g, 84%) as needles, m.p. 89.5–90.5 °C (Found: C, 71.7; H, 6.95; P, 10.5. $C_{18}H_{21}O_2$ requires C, 72.0; H, 7.05; P, 10.3%); R_F (EtOAc) 0.42, ν_{max}(Nujol mull)/cm^{-1} 3350 (OH), 1440 (PPh) and 1180 (P=O); $\delta_H(CDCl_3)$ 7.9–7.4 (10 H, m, Ph_2PO), 5.75 (1 H, dq, *J* 16 and 7, CH=C*H*Me), 5.33 (1 H, s, OH), 5.25 (1 H, d, *J* 16, C*H*=CH), 2.6 (2 H, d, J_{PH} 10, PCH_2), 1.3 (3 H, s, Me) and 1.3 (3 H, d, *J* 7, CHMe); *m/z* 300 (2%, M^+), 285 (40, M − Me), 282 (20, M − H_2O), 216 [65, $Ph_2P(OH)CH_2^+$], 215 (100, $Ph_2POCH_2^+$), 202 (20, Ph_2POH) and 201 (85, Ph_2PO).

(E)-5-*Diphenylphosphinoyldec*-2-*en*-4-*ol* **23e**.—Butyllithium (1.5 mol dm^{-3} in hexane) was added dropwise to a stirred solution of hexyldiphenylphosphine oxide[17] (42.9 g) in THF (550 ml) at 0 °C under nitrogen to give permanent anion colour. Butyl-lithium (105 ml) was added at between 0 and −10 °C. The solution was cooled to −60 °C, and freshly distilled crotonaldehyde (11.0 g) was added dropwise over 20 min. The solution was warmed to 0 °C over 15 min and saturated aqueous ammonium chloride (50 ml) added. The solvent was evaporated under reduced pressure, water (400 ml) was added, and the mixture was extracted with dichloromethane (3 × 200 ml). The combined organic extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give a crystalline mixture of diastereoisomers (53 g, 98%). Fractional crystallisation of 35 g and flash chromatography[19] on silica, eluting with 1:1 EtOAc–hexane followed by EtOAc gave the less soluble 4RS,5RS-*diastereoisomer* (10.28 g, 29%), m.p. 171.5–172 °C (from 3:1 EtOAc–hexane) (Found: C, 73.9; H, 8.3. $C_{22}H_{29}O_2P$ requires C, 74.1; H, 8.15%); R_F (2:1 EtOAc–hexane) 0.21; ν_{max}/cm^{-1} 3350 (OH), 1440 (PPh) and 1160 (P=O); $\delta_H(CDCl_3)$ 7.3–8.0 (10 H, m, Ph_2PO), 5.65 (1 H, dq, *J* 16 and 6, MeCH=CH), 5.35 (1 H, dd, *J* 16 and 6, MeCH=C*H*), 4.7 (1 H, br s, OH), 4.48 (1 H, dt, J_{PH} 18.5 and J_{HH} 5.5, C*H*OH), 2.2–2.7 (1 H, m, PCH), 1.43 (3 H, d, *J* 6, MeCH), 1.0–2.0 [8 H, m, $(CH_2)_4$] and 0.76 (3 H, t, *J* 7, $MeCH_2$); *m/z* 356 (2%, M^+), 338 (M − H_2O), 286 [44, $Ph_2P(OH)CH(CH_2)_4Me$], 229 (100, $Ph_2POCH{=}CH_2$), 202 (93, Ph_2POH) and 201 (38, Ph_2PO) and the more soluble 4RS,5SR-*diastereoisomer*, (20.3 g, 57%), m.p. 108–109 °C (from 1:3 EtOAc–hexane) (Found: C, 74.2; H, 8.2. $C_{22}H_{29}O_2P$ requires C, 74.1; H, 8.15%), R_F (2:1 EtOAc–hexane) 0.27; ν_{max}/cm^{-1} 3400 (OH), 1440 (PPh) and 1160 (P=O); $\delta_H(CDCl_3)$ 7.3–8.0 (10 H, m, Ph_2PO), 5.70 (1 H, dq, *J* 16 and 6, MeC*H*=CH), 5.46 (1 H, dd, *J* 16 and 6, MeCH=C*H*), 4.80 (1 H, br s, OH), 4.57 (1 H, br ddd, J_{PH} 13, J_{HH} 4 and 2, C*H*OH), 2.2–2.5 (1 H, m, PCH), 1.63 (3 H, d, *J* 6, MeCH), 0.9–2.0 [8 H, m, $(CH_2)_4$] and 0.72 (3 H, t, *J* 7, $MeCH_2$); $\delta_C(CDCl_3)$ 13.7 (q, $MeCH_2$), 17.48 (q, MeCH), 21.97 and 22.18 (2 t, $MeCH_2CH_2$), 29.57 (dt, J_{PC} 6.9, $PCHCH_2CH_2$), 31.55 (t, $PCHCH_2$), 43.19 (dd, J_{PC} 68.0, PCH), 70.52 (d, CHOH), 126.51 (d, CH=) and 128.34–133.0 (11 C, m, Ph_2PO and CJH=) (Found: M^+, 356.1904. $C_{22}H_{29}O_2P$ requires M 356.1905); *m/z* 356 (2%, M^+), 338 (5, M − H_2O), 286 [53, $Ph_2P(OH)CH(CH_2)_4Me$], 229 (98, $Ph_2POCH{=}CH_2$), 202 (100, Ph_2POH) and 201 (55, Ph_2PO).

(E)-5-*Diphenylphosphinoyl*-4-*methyldec*-2-*en*-4-*ol* E-**23f**.—Butyllithium (1.5 mol dm^{-3} solution in hexane) was added dropwise to a stirred solution of hexyldiphenylphosphine oxide[17] (1.44 g) in dry ether (50 ml) under nitrogen at 0 °C until a permanent anion colour formed, then further butyllithium (3.5 ml) was added. A solution of pent-3-en-2-one (0.43 g) in dry ether (10 ml) was added over 5 min. After 10 min, saturated aqueous ammonium chloride (20 ml) was added, the layers were separated, and the aqueous layer was extracted with ether (3 × 20 ml). The combined organic fractions were dried and evaporated under reduced pressure to give an oil which was purified by flash chromatography[19] on silica, eluting with CH_2Cl_2–ether (3:1) to give the alcohol (1.2 g, 65%) as a mixture of diastereoisomers, rearranged directly to the alcohol *E*-**25f** below.

1-*Diphenylphosphinoylbut*-3-*en*-2-*yl Acetate* **26a**.—A solution of toluene-*p*-sulphonic acid (0.18 g) in acetic acid (5 ml) and acetic anhydride (2 ml) was added to a stirred solution of the alcohol **23a** in acetic acid (5 ml) at room temperature. After 20 h, the reaction mixture was poured into water (70 ml) and extracted with dichloromethane (3 × 20 ml). The combined organic extracts were washed with dilute ammonia (20 ml), water (2 × 20 ml) and brine (2 × 20 ml) and dried (Na_2SO_4). The solvent was removed under reduced pressure. Flash column chromatography[19] on silica, eluting with ethyl acetate gave the acetate (600 mg, 86%) as needles, m.p. 121–122 °C (from EtOAc) (Found: C, 68.6; H, 6.15; P, 9.9. $C_{18}H_{19}PO_3$ requires C, 68.8; H, 6.2; P, 9.85%); R_F (EtOAc) 0.42; ν_{max}(Nujol)/cm^{-1} 1740 (ester), 1420 (PPh) and 1200 (P=O); $\delta_H(CDCl_3)$ 8.0–7.3 (10 H, m, Ph_2PO), 5.97 (1 H, ddd, *J* 17, 11 and 7, CHC*H*=CH_2), 5.9–5.55 (1 H, m, C*H*CH=CH_2), 5.20 (1 H, d, *J* 17, CH=CH_AH_B), 5.15 (1 H, d, *J* 11, CH=CH_AH_B) and 3.0–2.5 [2 H, m, $Ph_2P(O)CH_2$]; *m/z* 255 (55%, M − OAc), 215 [15, $Ph_2P(O)CH_2$], 202 (30, Ph_2POH) and 201 (100, Ph_2PO).

Allylic Rearrangement by Method A (*Table 1*): 3-*Acetoxy*-1-*diphenylphosphinoylpent*-2-*ene* **24b**.—The alcohol **23b** (4.29 g) in acetic acid (38 ml) was added to a stirred solution of toluene-*p*-sulphonic acid (TsOH) (900 mg) in acetic acid (38 ml) and acetic anhydride (15 ml) at 0 °C. After 18 h at room temperature, the solution was poured into water (700 ml) and extracted with dichloromethane (4 × 100 ml). The organic fractions were washed with dilute aqueous ammonia (2 × 100 ml), water (100 ml) and brine (2 × 50 ml) and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue purified by column chromatography on silica, eluting with EtOAc to give the *acetate* (4.06 g, 82%); $\delta_H(CDCl_3)$ 7.9–7.4 (10 H, m, Ph_2PO), 6.0–6.55 (1 H, m CH=), 5.45–5.1 (1 H, m, CH=), 3.15 (2 H, dd, J_{HP} 14, J_{HP} 6, PCH_2), 1.90 (3 H, s, OAc) and 1.10 (3 H, *J* 7, CHMe) (Found: M^+ 328.1237. $C_{19}H_{21}O_3P$ requires M 328.1229); *m/z* 328 (4%, M^+), 269 (15, M − OAc), 202 (40, Ph_2POH) and 201 (100, Ph_2PO).

(E)- *and* (Z)-1-*Acetoxy*-4-*diphenylphosphinoyl*-3-*methylbut*-2-*ene* **24c**.—In the same way, the alcohol **23c** (4 g) gave *Z*-**24c** (2.12 g, 46%) as needles, m.p. 95.5–97 °C (from EtOAc) (Found: C, 69.5; H, 6.45; P, 9.5. $C_{19}H_{21}O_3P$ requires C, 69.5; H, 6.45; P, 9.4%); R_F (EtOAc) 0.42; ν_{max}(Nujol)/cm^{-1} 1745 (ester), 1600 (Ph), 1450 (P–Ph) and 1260 and 1200 (P=O); $\delta_H(CDCl_3)$ 8.0–7.4 (10 H, m, Ph_2PO), 5.5 (1 H, m, =CH CH_2OAc), 4.2 (2 H, d, *J* 7, CH_2OAc), 3.3 (2 H, d, J_{HP} 13, PCH_2), 1.95 (3 H, s, OAc) and 1.8 (3 H, br s, MeC=); *m/z* 328 (14%, M^+), 269 (20 M − OAc), 268 (65, M − HOAc), 202 (70, Ph_2POH) and 201 (100, Ph_2PO); and *E*-**24c** (2.15 g, 47%) as needles, m.p. 95.5–96 °C (from EtOAc) (Found: C, 69.2; H, 6.45; P, 9.3. $C_{19}H_{21}O_3P$ requires C, 69.5; H, 6.45; P, 9.4%); R_F(EtOAc) 0.33; ν_{max}(Nujol)/cm^{-1} 1725 (ester) and 1440 (P–Ph); $\delta_H(CDCl_3)$

8.0–7.3 (10 H, m, Ph_2PO), 5.3 (1 H, m, CH=), 4.45 (2 H, m, CH_2OAc), 3.1 (2 H, d, J_{HP} 15, PCH_2), 1.93 (3 H, s, OAc) and 1.8 (3 H, br s, MeC=); *m/z* 328 (3%, M^+), 269 (18, M − OAc), 268 (55, M − HOAc), 202 (50, Ph_2POH) and 201 (100, Ph_2PO).

(E)- *and* (Z)-2-*Acetoxy*-5-*diphenylphosphinoyl*-4-*methylpent*-3-*ene* **24d**.—In the same way, the alcohol **23d** (6 g) gave *Z*-**24d** (3.15 g, 46%) as needles, m.p. 106.5–107.5 °C (from EtOAc) (Found: C, 70.2; H, 6.75; P, 8.8. $C_{20}H_{23}O_3P$ requires C, 70.2; H, 6.75; P, 9.1%); R_F(EtOAc) 0.42; ν_{max}(Nujol)/cm^{-1} 1740 (ester), 1450 (P–Ph) and 1190 (P=O); δ_H($CDCl_3$) 7.95–7.35 (10 H, m, Ph_2PO), 5.2 (2 H, m, MeC*H*OAc and C=CH), 3.85 (1 H, dd, J_{HH} 14, J_{PH} 12, PCH_AH_B), (1 H, t, J_{HH} = J_{PH} 14, PCH_AH_B), 1.93 (3 H, s, OAc), 1.75 (3 H, d, *J* 3, MeC=) and 0.8 (3 H, d, *J* 6, MeCHOAc); *m/z* 342 (1%, M^+), 299 (10, M − Ac), 283 (24, M − OAc), 282 (74, M − AcOH), 267 (20, 282 − Me), 202 (Ph_2POH) and 201 (100, Ph_2PO); and *E*-**24d** (3.11 g, 45%) as needles, m.p. 121.5–123 °C (from EtOAc) (Found: C, 69.6; H, 6.75; P, 8.9. $C_{20}H_{23}O_3P$ requires C, 70.2; H, 6.75; P, 9.1%); R_F(EtOAc) 0.31; ν_{max}(Nujol)/cm^{-1} 1735 (ester) and 1145 (P–Ph); δ_H($CDCl_3$) 7.0–7.3 (10 H, m, Ph_2PO), 5.5 (1 H, m, MeC*H*OAc), 3.1 (2 H, d, J_{HP} 14, PCH_2), 1.93 (3 H, s, OAc), 1.8 (3 H, br s, MeC=) and 1.03 (3 H, d, *J* 7, MeCH); *m/z* 283 (10%, M − OAc), 282 (30, M − AcOH), 267 (10, 282 − Me), 202 (50, Ph_2POH) and 201 (100, Ph_2PO).

(E)-2-*Acetoxy*-4-*diphenylphosphinoyldec*-3-*ene* E-**24e**.—In the same way, the alcohol **23e** (17.6 g) gave a 1:1 mixture of diastereoisomers of the acetates as a colourless oil, R_F(EtOAc–hexane, 1:2) 0.21; ν_{max}/cm^{-1} 1725 (C=O) and 1442 (P–Ph); δ_H($CDCl_3$) 7.3–7.9 (10 H, m, Ph_2PO), 5.0–5.6 (3 H, m, C*H*=C*H*C*H*OAc), 2.8–3.0 (1 H, m, PH), 1.93 and 1.94 (3 H, two s, Ac), 1.0–2.1 [8 H, m, $(CH_2)_4$] and 1.0 and 1.05 (3 H, two t, *J* 6.4, $MeCH_2$) (Found: M^+ 398.2020. $C_{24}H_{31}O_3P$ requires M 398.2011); *m/z* 398 (11%, M^+), 339 (5, M − OAc), 338 (5, M − AcOH), 219 (66), 202 (40, Ph_2POH) and 201 (100, Ph_2PO). The alcohols **25e** and their esters were fully characterised as individual diastereoisomers.[13,16]

(E)-2-*Acetoxy*-5-*diphenylphosphinoyl*-4-*methyldec*-3-*ene* E-**24f**.—In the same way, the alcohol **23f** (0.75 g) gave a 1.7:1 mixture of diastereoisomers of the acetates (0.49 g, 60%) (Found: M^+ 412.2169. $C_{23}H_{33}O_3P$ requires M 412.2167); *m/z* 412 (5%, M^+), 352 (88, M − AcOH) and 201 (100, Ph_2PO). The alcohols **25f** and their esters were fully characterised as individual diastereoisomers.[13,16]

Allylic Rearrangement of E-**23f** *in Acid*.—Dilute HCl (20 ml) was added to a solution of *E*-**23f** (2.5 g) in dioxane (50 ml) at room temperature (method of Braude and Stern).[18] The solution was stirred for 10 min and extracted with dichloromethane (3 × 25 ml). The organic fractions were dried (Na_2SO_4) and evaporated under reduced pressure to give a 2:1 mixture of diastereoisomers of **25f** as an oil.

Oxidative Allylic Rearrangement of the Allylic Alcohols **23**: (E)-5-*Diphenylphosphinoyl*-4-*methyl*-3-*en*-2-*one* **28**.—A solution of **23f** (0.7 g) in dichloromethane (2 ml) was added to pyridinium chlorochromate (0.41 g) in dichloromethane (3 ml) at room temperature. After 2 h ether (5 ml) was added, the ether layer removed, and the black resinous residue washed with ether (3 × 2 ml). The organic fractions were washed with NaOH (2 mol dm^{-3}; 10 ml), HCl (2 mol dm^{-3}; 10 ml) and saturated $NaHCO_3$ (2 × 5 ml), dried and evaporated under reduced pressure. The oil was purified on silica, eluting with EtOAc–hexane (4:1) to give the enone (0.42 g, 60%), m.p. 138–140 °C (from EtOAc–hexane) (Found: C, 75.2; H, 7.95. $C_{23}H_{29}O_2P$ requires C, 75.0; H, 7.9%); R_F 0.46; ν_{max}(Nujol)/cm^{-1} 1685 and 1612 (C=C–C=O), 1439 (P–Ph) and 1191 (P=O); δ_H($CDCl_3$) 8.1–7.3 (10 H, m, Ph_2PO), 6.13 (1 H, br d, J_{PH} 4, CHCO), 2.95 (1 H, m, PCH), 2.06 (3 H, dd, J_{PH} 2.5 and J_{HH} < 1, MeC=), 2.00 (3 H, s, MeCO), 1.0–2.0 [8 H, m, $(CH_2)_4$] and 0.80 (3 H, t, *J* 6, $MeCH_2$), irradiation at δ 6.13 caused an 11% NOE at δ 2.95; δ_C($CDCl_3$) 13.96 (q, $MeCH_2$), 19.79 (q, MeC=), 22.38 (t, $MeCH_2$), 27.50 (t, $MeCH_2CH_2$), 27.77 (dt, J_{CP} 13.0, $PCHCH_2CH_2$), 31.41 (t, $PCHCH_2$), 31.81 (q, MeCO), 51.80 (dd, J_{CP} 64.4, PCH), 128.34–131.97 (11 C, m, Ph_2PO and MeC=*C*), 152.38 (s, Me*C*=C) and 197.98 (s, CO) (Found: M^+, 368.1915. $C_{23}H_{29}O_2P$ requires M, 368.1905); *m/z* 368 (11%, M^+), 325 (45, M − Ac), (100, $Ph_2PO_2H_2$) and 201 (80, Ph_2PO); λ_{max}(EtOH)/nm 205, (ε 24 700), 226 (ε 20 700) and 248 (ε 12 600).

(E)-1-*Diphenylphosphinoylpent*-2-*en*-4-*ol* E-**25b**.—Potassium carbonate (7.5 g) in water (30 ml) was added dropwise to a stirred solution of the rearranged acetate **24b** (5.9 g) in methanol (100 ml) at room temperature. After 15 h, the solution was poured into water (100 ml) and extracted with dichloromethane (3 × 100 ml). The organic extracts were washed with brine (70 ml) dried (Na_2SO_4) and evaporated under reduced pressure. Column chromatography on silica, eluting with EtOAc gave the *alcohol* (4.43 g, 86%) as an oil, R_F (EtOAc–EtOH, 10:1) 0.30; δ_H 8.0–7.4 (10 H, m, Ph_2PO), 5.9–5.4 (2 H, m, CH=CH), 4.2 (1 H, m, C*H*OH), 3.45 (1 H, s, OH), 3.1 (2 H, dd, J_{HH} 14, J_{HP} 6, CH_2P) and 1.07 (3 H, d, *J* 7, CHMe) (Found: M^+, 286.1121. $C_{17}H_{19}O_2P$ requires M, 286.1123); *m/z* 286 (4%, M^+), 271 (15, M − Me), 268 (10, M − H_2O), 241 (15, M − MeCHO), 202 (40, Ph_2POH) and 201 (100, Ph_2PO).

General Procedure for the Hydrolysis of the Rearranged Acetates **24**: (E)-4-*Diphenylphosphinoyl*-3-*methylbut*-2-*en*-1-*ol* E-**25c**.—Sodium hydroxide (10% w/w solution; 14 ml) was added in one portion to a stirred solution of the acetate *E*-**24c** (9.1 g) in methanol (140 ml) at 0 °C. After 2.5 h at 0 °C, aqueous ammonium chloride (20 ml) was added. The methanol was removed under reduced pressure and the solution extracted with dichloromethane (4 × 40 ml). The organic extracts were dried (Na_2SO_4) and evaporated under reduced pressure. Recrystallisation from EtOAc gave the *alcohol* (5.99 g, 76%) as needles, m.p. 107.5–108.5 °C (Found: C, 71.0; H, 6.5; P, 10.8. $C_{17}H_{19}O_2P$ requires C, 71.3; H, 6.7; P, 10.8%); R_F(EtOAc) 0.19; ν_{max}(Nujol)/cm^{-1} 3250 (OH) and 1440 (P–Ph); δ_H($CDCl_3$) 8.0–7.4 (10 H, m, Ph_2PO), 5.4 (1 H, m, CH=), 4.05 (2 H, m, CH_2OAc), 3.2 (1 H, s, OH), 3.1 (2 H, d, J_{HP} 14, PCH_2) and 1.65 (3 H, br s, MeC=); *m/z* 286 (7%, M^+), 268 (50, M − H_2O), 202 (50, Ph_2POH) and 201 (100, Ph_2PO). Irradiation of the methyl signal at δ 1.65 caused no NOE on the signal at δ 5.4.

(Z)-4-*Diphenylphosphinoyl*-3-*methylbut*-2-*en*-1-*ol* Z-**25c**.—In the same way, the acetate *Z*-**24c** (3.78 g) gave, after chromatography on silica, eluting with EtOAc, an impurity, probably 1-diphenylphosphinoyl-2-methylbutadiene from its NMR spectrum, and the *alcohol* (2.03 g, 62%) as prisms, m.p. 118–119 °C (from EtOAc) (Found: C, 71.3; H, 6.55; P, 10.5. $C_{17}H_{19}O_2P$ requires C, 71.3; H, 6.7; P, 10.8%); R_F (EtOAc) 0.27; ν_{max}(Nujol)/cm^{-1} 3260 (OH) and 1440 (P–Ph); δ_H($CDCl_3$) 8.0–7.4 (10 H, m, Ph_2PO), 5.9 (1 H, m, CH=) 4.5 (1 H, br s, OH), 4.05 (2 H, d, *J* 7, CH_2OAc), 3.3 (2 H, d, J_{HP} 14, PCH_2) and 1.35 (3 H, br s, MeC=); *m/z* 286 (18%, M^+), 268 (35, M − H_2O), 202 (100, Ph_2POH) and 201 (90, Ph_2PO). Irradiation at δ 1.35 gave a positive NOE of 9 ± 2% at δ 5.9.

(E)-1-*Diphenylphosphinoyl*-2-*methylpent*-3-*en*-4-*ol* E-**25d**.—In the same way, the acetate *E*-**24d** (2.86 g) gave the *alcohol* (2.0 g, 80%) as needles, m.p. 138–139 °C (from EtOAc) (Found: C, 71.6; H, 7.05; P, 10.5. $C_{18}H_{21}O_2P$ requires C, 72.0; H, 7.05;

P, 10.5%); R_F (EtOAc–EtOH, 6:1) 0.41; ν_{max}(Nujol)/cm^{-1} 3310 (OH) and 1450 (P–Ph); δ_H($CDCl_3$) 8.0–7.3 (10 H, m, Ph_2PO), 5.1 (1 H, m, CH=), 4.5 (1 H, quintet, *J* 7, C*H*Me), 3.05 (2 H, d, J_{HP} 13, PCH_2), 2.7 (1 H, s, OH), 1.75 (3 H, d, *J* 3, MeC=) and 0.95 (3 H, d, *J* 7, MeCH); *m/z* 282 (51%, M − H_2O), 267 (10, 282 − Me), 253 (53), 202 (60, Ph_2POH) and 201 (100, Ph_2PO).

(Z)-1-*Diphenylphosphinoyl*-2-*methylpent*-3-*en*-4-*ol* Z-**25d**.—In the same way, the acetate *Z*-**24d** (3.15 g) gave the alcohol (2.23 g, 80%) as needles, m.p. 121–122 °C (Found: C, 71.7; H, 7.0; P, 10.5. $C_{18}H_{21}O_2P$ requires C, 72.0; H, 7.05; P, 10.5%); R_F(EtOAc–EtOH, 6:1), 0.53; ν_{max}/cm^{-1} 3260 (OH) and 1440 (P–Ph); δ_H($CDCl_3$) 8.0–7.3 (10 H, m, Ph_2PO), 5.5 (1 H, m, CH=), 4.3 (1 H, br s, OH), 4.25 (1 H, dq, *J* 7 and 6, MeC*H*O), 3.4 (1 H, dd, J_{HH} 14 and J_{HP} 19, PCH_AH_B), 2.9 (1 H, dd, J_{HH} 14 and J_{HP} 9, PCH_AH_B), 1.25 (3 H, d, *J* 2, MeC=) and 1.15 (3 H, d, *J* 6, MeCH); *m/z* 300 (15%, M$^+$), 284 (21), 282 (25, M − H_2O), 257 (7), 255 (9), 216 (7), 215 (9), 202 (100, Ph_2POH) and 201 (95, Ph_2PO).

Horner–Wittig Reactions: (E)-1-*Diphenylphosphinoyl*-1-(1-*hydroxycyclohexyl*)-2-*methylbut*-2-*en*-4-*ol* E-**29**.—Butyllithium (1.6 mol dm^{-3} solution in hexane; 4.4 ml) was added dropwise to a stirred solution of the alcohol *E*-**25c** (1 g) in dry THF (40 ml) under nitrogen at −78 °C. After 15 min, a solution of cyclohexane (390 mg, passed down a short column of alumina UG 1 immediately before use) in THF (2 ml) was added dropwise over 2 min. The mixture was allowed to warm rapidly to 0 °C and saturated aqueous ammonium chloride (10 ml) was added. The aqueous layer was separated and extracted with EtOAc (3 × 30 ml). The combined organic fractions were dried (Na_2SO_4) and evaporated under reduced pressure. Flash chromatography[19] on silica, eluting with EtOAc, gave the *diol* (1.07 g, 78%) as needles, m.p. 159–160 °C (from EtOAc); R_F (EtOAc) 0.37 (Found: C, 71.7; H, 7.65; P, 7.9. $C_{23}H_{29}O_3P$ requires C, 71.8; H, 7.6; P, 8.1%); δ_H($CDCl_3$) 8.3–7.3 (10 H, m, Ph_2PO), 5.65 (1 H, m, CH=), 4.0 (2 H, m, CH_2OH), 3.45 (1 H, d, J_{HP} 11, CHP) and 1.8–1.3 [13 H, m, MeC= and $(CH_2)_5$] (Found: M$^+$, 384.1856. $C_{23}H_{29}O_3P$ requires M, 384.1854); *m/z* (384 (2%, M$^+$), 286 (70, M − $C_6H_{10}O$), 268 (100), 202 (100, Ph_2POH) and 201 (70, Ph_2PO).

(E)-1-*Diphenylphosphinoyl*-1-(1-*hydroxycycloheptyl*)*pent*-2-*en*-4-*ol* E-**31**.—In the same way, *E*-**25b** (830 mg, 2.9 mmol) and cycloheptanone (400 mg, 3.6 mmol) gave recovered *E*-**25b** (200 mg, 23%) and the *diol* as a 1:1 mixture of diastereoisomers (600 mg, 50%), m.p. 164–165 °C (from EtOAc); R_F(EtOAc) 0.38; δ_H($CDCl_3$) 8.2–7.4 (10 H, m, Ph_2PO), 5.9–5.2 (2 H, m, CH=CH), 4.1 (1 H, m, C*H*OH), 3.6 (2 H, br s, OH), 3.5–3.2 (1 H, 2 d, J_{HP} 11 and 3.25, PCH), 1.85–1.15 [12 H, m, $(CH_2)_6$], 1.05 and 0.95 (3 H, 2 d, *J* 7 Hz, CHMe) (Found: M$^+$, 398.1996. $C_{24}H_{31}O_3P$ requires M, 398.2011); *m/z* 398 (1%, M$^+$), 286 (40), 268 (37), 254 (20), 242 (30), 219 (20), 202 (65, Ph_2POH) and 201 (100, Ph_2PO).

Horner–Wittig Eliminations: (E)-1-*Cyclohexylidene*-2-*methylbut*-2-*en*-4-*ol* E-**30**.—The diol *E*-**29** (380 mg) in dry DMF was added to a stirred suspension of sodium hydride (50% dispersion in oil, washed with dry hexane; 200 mg) in dry DMF (10 ml) at 50 °C under nitrogen. After 3.25 h, a white precipitate had appeared and the mixture was cooled to room temperature and aqueous ammonium chloride (5 ml) added dropwise. Water (10 ml) was added, the mixture was extracted with ether (3 × 30 ml), and the combined extracts were washed with water (3 × 70 ml) and brine (70 ml), dried (Na_2SO_4) and evaporated under reduced pressure. Preparative TLC on silica eluting with light petroleum (b.p. 60–80 °C)–EtOAc (3:1) gave the *diene alcohol* (120 mg, 75%); R_F[light petroleum (b.p. 60–80 °C)–EtOAc (3:1)] 0.41; δ_H($CDCl_3$) 5.6 (1 H, s, CH=), 5.47 (1 H, t, *J* 7, =C*H*CH_2), 4.20 (2 H, d, *J* 7, CH_2O), 2.6–2.2 (4 H, m, allylic CH_2s), 1.85 (3 H, br s, MeC=) and 1.75–1.5 [6 H, n, $(CH_2)_3$] (Found: M$^+$, 166.1325. $C_{11}H_{18}O$ requires M, 166.1358); *m/z* 166 (50%, M$^+$), 151 (25, M − Me), 148 (55, M − H_2O), 135 (30), 133 (45), 121 (50), 105 (100), 95 (50), 93 (70), 91 (90), 81 (70), 79 (75), 77 (40), 69 (20), 67 (60) and 55 (55).

Cycloheptylidenepent-2-*en*-4-*ol* E-**32**.—In the same way, *E*-**31** (200 mg) gave the diene alcohol (70 mg, 76%); R_F[light petroleum (b.p. 60–80 °C)–EtOAc (3:1)] 0.27; δ_H($CDCl_3$) 6.2 (1 H, d, *J* 8, C=C*H*CH=CH), 5.65 (1 H, dd, *J* 8, 14, C=CHC*H*=CH), 5.5 [1 H, dd, *J* 7, 14, C=CHCH=C*H*CH(OH)], 4.25 ([1 H, quintet, *J* 7, =CHC*H*Me(OH)], 2.2 (5 H, m, OH and allylic CH_2s), 1.8–1.4 [8 H, m, $(CH_2)_4$] and 1.35 (3 H, d, *J* 7, *Me*CH).

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