

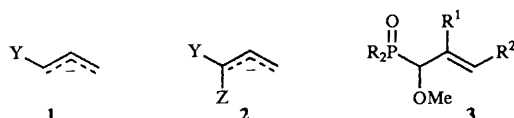
Preparation of α -methoxyallylphosphonates and their conversion into 2-methoxyalka-1,3-dienes

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A range of α -alkoxyphosphonates, including novel α -methoxyallyl phosphonates have been prepared from acetals. The latter have been used to provide an efficient and convenient synthesis of conjugated methoxy dienes, in which *E*-geometry predominates in the newly formed double bond but the geometry of the original allyl system is preserved.

The chemistry of allylic anions containing α -heteroatom substituents [cf. 1, 2; e.g. Y, Z = SiR₃, SR, OR, NR₂, P(O)R₂]



has been intensively investigated over the years and has led to the development of many new synthetic methods.¹ Regiochemical control in reactions of these ambident anions with electrophiles is crucial to the utility of these methods, and a number of factors² have been identified as important influences on site selectivity. Previously, we described³ the preparation of a series of α -methoxyallylphosphine oxides 3 (R = Ph) and the results of some single⁴ and double⁵ electrophilic quenching reactions of the anions derived from these oxides. In general, this work indicated that the reactions of the lithium anions of 3 (R = Ph), with electrophiles, including aldehydes, proceeds with predominant γ -regioselectivity. Preferential reaction of the anions with aldehydes, at the α -position of the allylic system, in a Wittig-Horner reaction to form 2-methoxy-1,3-dienes, required either the presence of bulky groups at the γ -position of the allylic double bond, or the initial preparation of the titanium ate complex.^{4b}

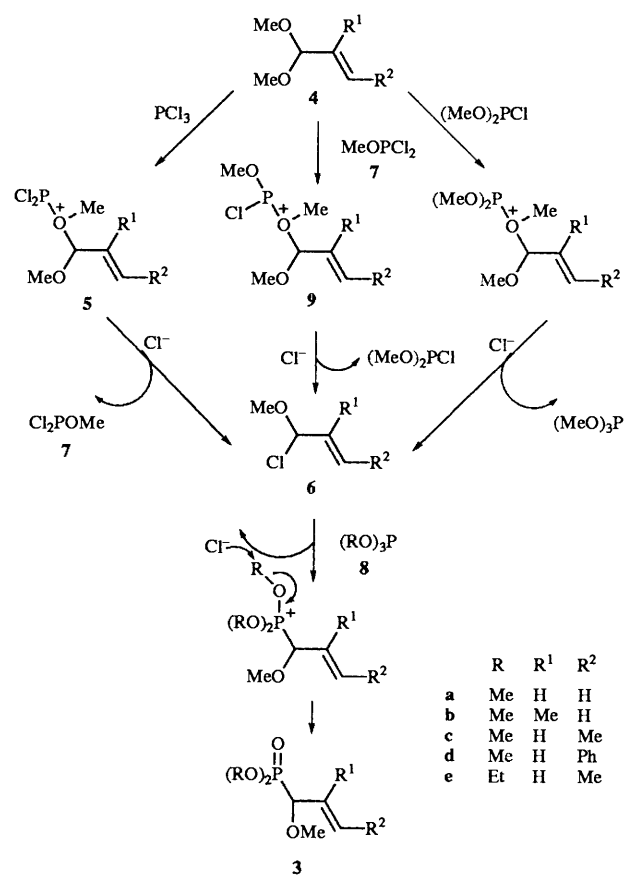
The major drawbacks in the phosphine oxide strategy were the lack of reactivity of these anions with ketones, and the apparent difficulty of obtaining good yields of conjugated methoxy dienes with aliphatic aldehydes. In view of the generally higher reactivity of phosphonates relative to phosphine oxides in Wittig-type reactions our efforts were directed towards the preparation of dimethyl α -methoxyallylphosphonates 3 (R = OMe).

In this paper, we describe in detail our study of the preparation of dimethyl α -methoxyallylphosphonates 3 (R = OMe) and their condensation reactions with carbonyl compounds.

Results and discussion

The preparation of dimethyl α -methoxyphosphonates and in particular dimethyl α -methoxyallylphosphonates 3 (R = OMe) was based on the known reaction⁶ of phosphorus(III) chloride or its partial esters with acetals, and our experience of the reaction of chlorodiphenylphosphine with allylic acetals to form α -methoxyallyldiphenylphosphine oxides. In that reaction the phosphorus reagent was considered to act both as an electron donor and an electron acceptor. Consequently, the possibility of using separate phosphorus reagents in the role of electron acceptor and electron donor was considered, and we

settled on treating a series of dimethyl acetals 4 with trimethyl phosphite and phosphorus trichloride in the ratio of 3:2:1. The mechanism proposed for this conversion, which illustrates why this ratio of reactants was required, is shown in Scheme 1. The



Scheme 1

first equivalent of dimethyl acetal 4 reacts with phosphorus trichloride displacing a chloride ion to produce intermediate 5 which reacts with chloride ion to afford 6 and methyl dichlorophosphite 7. Intermediate 6 now reacts with trimethyl phosphite 8 (R = Me) to yield, via an Arbuzov reaction, the desired phosphonate 3a-d. Methyl dichlorophosphite 7 produced in the above process, now acts as an electron acceptor in the reaction with a second equivalent of acetal (4 → 9 → 6) leading to the phosphonate. These first two cycles use up the 2 equivalents of trimethyl phosphite, so the final equivalent of acetal reacts with the trimethyl phosphite which is generated

Table 1 Methoxy dienes from dimethyl α -methoxyallylphosphonates

Reagents: i, 1.2 equiv. LDA, 0.85 equiv. R^3R^4CO added in sequence

Phosphonate	R^3	R^4	1,3-Diene		
			Product	Yield (%) ^a	<i>EE:EZ</i> ^b
3a	<i>p</i> -MeOC ₆ H ₄	H	10	89	2:1
	Ph	Me	11	53	3:1
	Me	Me	12	45	—
3b	<i>p</i> -MeOC ₆ H ₄	H	13	74	2:1
	Ph	Me	14	67	> 10:1
3c	<i>p</i> -MeOC ₆ H ₄	H	15	65	2:1
	Bu	H	16	81	3:2
	Ph	Me	17	72	20:1
3d	<i>p</i> -MeOC ₆ H ₄	H	18	87	3:1
	Bu	H	19	68	3:1
	Ph	Me	20	94	> 10:1
	Me	Me	21	82	—
	Ph	Ph	22	90	—

^a Yields quoted are after chromatography. ^b ¹H NMR assay.

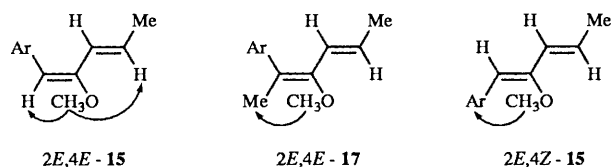


Fig. 1 Enhancements are obtained for those nuclei at the arrow-heads on irradiating those at the arrow-tails

in situ. In support of the proposed mechanism, reaction of 3 equivalents of crotonal dimethyl acetal ($R^1 = H$, $R^2 = Me$) with 1 equivalent of phosphorus trichloride and 2 equivalents of triethyl phosphite ($R = Et$) yielded the diethyl phosphonate **3e** along with significant amounts of the corresponding dimethyl phosphonate **3c**, thus confirming the *in situ* generation and subsequent reaction of trimethyl phosphite in the overall process.

Preparative details, and spectroscopic evidence for the structure assignments of these dimethyl α -methoxyallylphosphonates are given in the Experimental section. For example, in **3d** the *trans*-cinnamyl entity (J_{HH} 16 Hz) is evident, and each vinylic proton displays appropriate coupling to phosphorus ($^3J_{PH}$ 6 and $^4J_{PH}$ 5.6 Hz). The ¹H NMR of the above shows the methine proton of the PCHOMe subunit as a double doublet with J_{PH} 14.2 Hz, while the ¹³C NMR shows coupling between phosphorus and the methoxy-bearing carbon (J_{PC} 170 Hz) and between phosphorus and the methoxy carbon (J_{PC} 13 Hz).

Our interest in these dimethyl α -methoxyallylphosphonates lay in their potential use for the preparation of 2-methoxy-1,3-dienes by way of the Horner–Wadsworth–Emmons reaction.⁷ Alkoxy dienes have found wide application in organic synthesis, notably in Diels–Alder reactions.⁸ Within this group, 2-methoxyalka-1,3-dienes hold a prominent position, but one which is somewhat limited by the difficulty of routes available for their preparation.⁹

In the present study, treatment of these allylic phosphonates with lithium diisopropylamide at low temperatures produced the corresponding α -phosphono carbanions which reacted readily with 0.85 equiv. of an aldehyde or ketone to afford the

conjugated methoxy dienes **10–22** in reasonable to good yields (Table 1). These dienes were isolated by extraction with diethyl ether followed by a wash with aqueous sodium hydrogen carbonate. Flash chromatography of the residue gave the dienes as a mixture of double-bond isomers, the isomer ratio being determined from NMR experiments. Where it was possible for *E* and *Z* geometry to exist in the newly formed double bond, both isomers were usually observed, although *E*-geometry was found to predominate. The formation of two geometric isomers is quite standard in Wittig-type reactions leading to enol ethers.^{3,10} No loss of stereochemical integrity was observed in the olefinic functionality of the phosphonate ylide; a complication that often arises when allylic phosphonium ylides are used.¹¹

The isomers formed *via* aldehydes were distinguished quite readily by their ¹H NMR spectra, where it was observed that the *E*-isomer of the newly formed double bond had the $CH=C(OMe)$ proton resonating at a lower field than that of the *Z*-isomer,^{10b,12} presumably the result of the methoxy group exercising a deshielding effect upon a vinyl proton which is situated on the same side of the double bond. Ketones which proved unreactive to the anions of the corresponding phosphine oxide analogues, also produced dienes in reasonable yields, presumably as a result of the increased nucleophilicity of phosphonate anions compared with the anions of phosphine oxides. Although the assignment of stereochemistry was not at all trivial for the resulting tetrasubstituted alkenes, the isomers were distinguished from difference NOE experiments (see Fig. 1). The NOE enhancements which were obtained were generally of the order of 10%. Thus, in products of the general type **15** and **17**, irradiation of the methoxy signal in the major isomer gave enhancement of the vinyl proton or the analogously placed methyl group signals. This effect was confirmed by irradiation of the vinyl proton or methyl signal and obtaining enhancement of the methoxy resonance. When the methoxy signal of the minor isomer **15** was irradiated, enhancement of a portion of the aromatic signal was observed. These effects define the stereochemistry of the newly formed double bond unambiguously, and establish that the major isomer is the 3/4*E* isomer. In cases where NOE studies were not carried out, the

stereochemistry of the newly formed double bond was assigned by analogy, using the difference of the methoxy proton position. The stereochemistry about the 1,2/3-double bond was assigned as *E* from the observed J_{HH} (14–17.4 Hz) coupling constants. Furthermore, the observed enhancement of the 1/2 proton signal on irradiation of the methoxy signal confirmed this stereochemistry.

It is normal for ylides derived from triphenylphosphonium, diphenylphosphinoyl, and dialkoxyphosphinoyl compounds to yield intermediate β -hydroxyphosphorus derivatives from carbonyl compounds¹³ and the isolation and separation of such diastereoisomers has provided a basis for stereospecific alkene synthesis.^{10b} In the present study no such intermediates were observed and the ease of the elimination step in the formation of the dienes (this occurs at temperatures below 0 °C) means that stereoselective diene preparation will be difficult to achieve without significant modification of the reaction conditions. However, in certain circumstances, particularly when the dienes are hydrolysed to enones,^{5b} or converted into 2-substituted cyclohexanones *via* Diels–Alder adduct formation and hydrolysis, this will not be important.

We have described a method for the preparation of novel dimethyl α -methoxyallylphosphonates and shown that the lithium anions of these compounds react with aldehydes and ketones at the α -position in a Horner–Wadsworth–Emmons-type reaction to provide a convenient one-step synthesis of conjugated methoxy dienes. The product dienes are mixtures of 3/4*E*- and 3/4*Z*-isomers in which the former predominate, but the geometry present in the original allyl system is preserved in the 1/2 double bond.

Experimental

Mps were determined on an Electrothermal melting-point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 298 machine; the spectra of oils were run neat. ¹H NMR spectra were recorded on a Bruker AM300/WB (300 MHz) spectrometer and ¹³C NMR were recorded on a Bruker AM300/WB (75.5 MHz) spectrometer. Unless otherwise stated, the samples were dissolved in CDCl₃ and the chemical shifts are expressed in ppm downfield from tetramethylsilane as internal standard. ¹³C NMR assignments were supported by DEPT experiments. ¹H NMR assignments were assisted by NOE difference, ¹H–¹H COSY and ¹H–¹³C heteronuclear correlation experiments. *J* Values are given throughout in Hz. Mass spectra were recorded on a VC705 Double Focussing Spectrometer.

General procedure for the preparation of dimethyl α -methoxyphosphonates

A solution of the appropriate dimethyl acetal (0.3 mol) in toluene (30 cm³) was added to phosphorus trichloride (0.135 mol) in toluene. The mixture became warm, and once the heat had subsided (*ca.* 5 min), trimethyl phosphite (0.24 mol) was added dropwise. A few bubbles were evolved during the reaction and were presumed to be the gradual release of chloromethane (δ 2.9, singlet). The mixture was stirred for 3 h at room temperature before being fractionally distilled under reduced pressure. The phosphonates were obtained as colourless liquids.

Dimethyl (1-methoxyethyl)phosphonate. Obtained as a colourless liquid (77%), bp 51 °C/0.8 mmHg [Found: C, 35.7; H, 7.9%; (M + H)⁺, 169.0625. C₅H₁₃O₄P requires C, 35.70; H, 7.80%; M + H, 169.0629]; $\nu_{\text{max}}/\text{cm}^{-1}$ 1250 (P=O) and 1100–1000 (P–O–C); δ_{H} 1.45 (3 H, dd, *J* 7 and 18, CHCH₃), 3.57 (3 H, s, COCH₃), 3.68 (1 H, m, PCH) and 3.88 (6 H, d, *J* 10, 2 × POCH₃); δ_{C} 71.72 (d, *J* 166, PCH), 57.27 (d, *J* 7.3, POCH₃), 51.56 (d, *J* 7.3, COCH₃) and 13.80 (CHCH₃).

Dimethyl (1-methoxyprop-2-enyl)phosphonate 3a. Obtained

as a colourless liquid (82%), bp 114 °C/18 mmHg (Found: C, 39.7; H, 7.1%; M⁺, 180.0543. C₆H₁₃O₄P requires C, 39.99; H, 7.28%; M, 180.0551); $\nu_{\text{max}}/\text{cm}^{-1}$ 1640 (C=C), 1260 (P=O) and 1100–1000 (P–O–C); δ_{H} 3.44 (3 H, s, COCH₃), 3.82 (6 H, d, *J* 10, 2 × POCH₃), 4.06 (1 H, dd, *J* 6 and 16, PCH), 5.34 (1 H, ddd, *J* 1.4, 5.1 and 10.2, CHCH=CH_{cis}), 5.37 (1 H, ddd, *J* 1.4, 6 and 17.2, CHCH=CH_{trans}) and 5.96 (1 H, dddd, *J* 4, 6.5, 10.2 and 17.2, CH=CH₂); δ_{C} 130.30 (d, *J* 1.8, CH=CH₂), 118.59 (d, *J* 6.4, CH=CH₂), 78.00 (d, *J* 168, PCH), 57.45 (d, *J* 6.4, POCH₃) and 52.47 (d, *J* 5.8, COCH₃).

Dimethyl (1-methoxy-2-methylprop-2-enyl)phosphonate 3b. Obtained as a colourless liquid (83%), bp 95 °C/3.5 mmHg (Found: C, 43.1; H, 7.6%; M⁺, 194.0714. C₇H₁₅O₄P requires C, 43.28; H, 7.79%; M, 194.0708); $\nu_{\text{max}}/\text{cm}^{-1}$ 1645 (C=C), 1260 (P=O) and 1100–1020 (P–O–C); δ_{H} 1.89 (3 H, d, *J* 1.4, CCH₃), 3.42 (3 H, s, COCH₃), 3.85 (6 H, d, *J* 10, 2 × POCH₃), 4.01 (1 H, d, *J* 16, PCH) and 5.23 (2 H, m, C=CH₂); δ_{C} 138.44 (d, *J* 3.6, C=CH₂), 114.85 (d, *J* 12, C=CH₂), 80.73 (d, *J* 166, PCH), 57.37 (d, *J* 12.6, POCH₃), 52.26 (d, *J* 6.4, COCH₃) and 17.56 (CH₃).

Dimethyl (1-methoxybut-2-enyl)phosphonate 3c. Obtained as a colourless liquid (75%), bp 138 °C/0.8 mmHg [Found: C, 43.0; H, 7.6%; (M + H)⁺, 195.0790. C₇H₁₅O₄P requires C, 43.28; H, 7.79%; M + H, 195.0786]; $\delta_{\text{max}}/\text{cm}^{-1}$ 1660 (C=C), 1250 (P=O) and 1100–1000 (P–O–C); δ_{H} 1.80 (3 H, dd, *J* 4 and 5.6, CCH₃), 3.41 (3 H, s, COCH₃), 3.80 (6 H, d, *J* 10, 2 × POCH₃), 4.06 (1 H, dd, *J* 8 and 16, PCH), 5.50 (1 H, m, CHCH₃) and 5.90 (1 H, m, CH=CHCH₃); δ_{C} 130.27 (d, *J* 6.8, CH=CHCH₃), 122.66 (d, *J* 3, CH=CHCH₃), 76.85 (d, *J* 168, PCH), 55.87 (d, *J* 6.4, POCH₃), 51.29 (d, *J* 7, COCH₃) and 15.86 (CCH₃).

Dimethyl (1-methoxy-3-phenylprop-2-enyl)phosphonate 3d. Obtained as a colourless liquid (88%), bp 148 °C/0.2 mmHg [Found: C, 56.1; H, 6.7%; (M + H)⁺, 257.0936. C₁₂H₁₇O₄P requires C, 56.23; H, 6.69%; M + H, 257.0942]; $\nu_{\text{max}}/\text{cm}^{-1}$ 1645 (C=C), 1250 (P=O) and 1100–1000 (P–O–C); δ_{H} 3.24 (3 H, s, COCH₃), 3.52 (6 H, d, *J* 10, 2 × POCH₃), 4.01 (1 H, dd, *J* 7 and 14.2, PCH), 6.02 (1 H, dd, *J* 5.6 and 16, CH=CHPh), 6.52 (1 H, dd, *J* 6 and 16, CH=CHPh) and 7.0–7.25 (5 H, m, Ph); δ_{C} 134.22 (d, *J* 10.6, CH=CHPh), 121.36 (d, *J* 1.5, CH=CHPh), 150.63, 145.93, 127.93, 125.98 (aromatic carbons), 78.07 (d, *J* 170, PCH), 57.75 (d, *J* 13, POCH₃) and 54.76 (d, *J* 7, COCH₃).

Diethyl (1-methoxybut-2-enyl)phosphonate 3e. Crotonal dimethyl acetal (0.1 mol), phosphorus trichloride (0.045 mol) and triethyl phosphite (0.08 mol) were allowed to react as in the general procedure. This gave a mixture of the title compound and the previously prepared phosphonate 3c in a ratio of 2:1. The title compound was obtained as a colourless liquid (48%), bp 145 °C/0.6 mmHg (Found: C, 48.3; H, 8.9. C₉H₁₉O₄P requires C, 48.62; H, 8.62%; $\nu_{\text{max}}/\text{cm}^{-1}$ 1260–1180 (P=O) and 1070–1030 (P–O–C); δ_{H} 1.30 (6 H, t, *J* 7.2, 2 × OCH₂CH₃), 1.74 (3 H, dd, *J* 4 and 5, CHCH₃), 3.30 (3 H, s, COCH₃), 3.85–4.30 (4 H, m, 2 × OCH₂CH₃), 5.50 (1 H, m, CHCH₃) and 5.90 (1 H, m, CH=CHCH₃); δ_{C} 133.10, 124.05 (CH=CH), 78.94 (d, *J* 170.2, PCH), 62.89 (d, *J* 7.5, POCH₂), 53.35 (d, *J* 6.4, COCH₃), 17.27 (POCH₂CH₃) and 15.11 (CCH₃).

General procedure for reaction of the anions of dimethyl α -methoxyallylphosphonates with aldehydes and ketones

The phosphonate (10 mmol) was dissolved in anhydrous THF (30 cm³) and slowly added to a solution of LDA (1.2 equiv.) in THF at –78 °C and the mixture stirred at this temperature for 2 h. The appropriate aldehyde or ketone (0.85 equiv.) in anhydrous THF (5 cm³) was added, and the mixture stirred a further 4 h at –78 °C before being allowed to warm to room temperature. Saturated aqueous NH₄Cl (25 cm³) was then added to it, the layers were separated, and the aqueous layer was thoroughly extracted with diethyl ether. The combined

organic layers were washed in turn with saturated aqueous NaHCO_3 and saturated aqueous NaCl , dried (MgSO_4) and evaporated under reduced pressure. Flash chromatography of the residue [alumina, 10% diethyl ether in light petroleum (bp 40–60 °C)] gave the methoxy diene as a mixture of *E,E* and *E,Z*-isomers.†

3-Methoxy-4-(4'-methoxyphenyl)buta-1,3-diene 10. Obtained as a pale yellow oil (89%) which was a 2:1 mixture of *3E* and *3Z* isomers. (Found: C, 75.5; H, 7.6%; M^+ , 190.0994). $\text{C}_{12}\text{H}_{14}\text{O}_2$ requires C, 75.75; H, 7.42%; M , 190.0994). *3E* isomer: δ_{H} 3.73 (3 H, s, OCH_3), 3.80 (3 H, s, ArOCH_3), 5.19 (1 H, dd, J 2.2 and 10.7 $\text{CCH}=\text{CH}_{\text{cis}}$), 5.70 (1 H, dd, J 2.2 and 17.2, $\text{CCH}=\text{CH}_{\text{trans}}$), 5.84 (1 H, s, ArCH), 6.59 (1 H, dd, J 10.7 and 17.2, $\text{CCH}=\text{CH}_2$) and 6.87, 7.14 (2 × 2 H, 2 × d, aromatic); δ_{C} 157.93 (ArCOCH_3), 153.30 (COCH_3), 136.04 (ArCH), 133.44, 128.95, 127.06, 117.03 (aromatic and alkenyl carbons), 115.47 ($\text{C}=\text{CH}_2$), 55.26 (ArOCH_3) and 54.79 (OCH_3); *3Z* isomer: δ_{H} 3.64 (3 H, s, OCH_3), 3.79 (3 H, s, ArOCH_3), 5.14 (1 H, dd, J 2.2 and 10.7, $\text{CCH}=\text{CH}_{\text{cis}}$), 5.48 (1 H, dd, J 2.2 and 17.2, $\text{CCH}=\text{CH}_{\text{trans}}$), 5.80 (1 H, s, ArCH), 6.22 (1 H, dd, J 10.7 and 17.2, $\text{CCH}=\text{CH}_2$) and 7.28 and 7.58 (2 × 2 H, 2 × d, aromatic).

3-Methoxy-4-phenylpenta-1,3-diene 11. Obtained as a pale yellow oil (53%) which was a 3:1 mixture of *3E* and *3Z* isomers (Found: C, 82.5; H, 7.9%; M^+ , 174.1045). $\text{C}_{12}\text{H}_{14}\text{O}$ requires C, 82.71; H, 8.10%; M , 174.1045). *3E* isomer: δ_{H} 2.10 (3 H, s, CCH_3), 3.65 (3 H, s, OCH_3), 5.00 (1 H, dd, J 2 and 10.9, $\text{CCH}=\text{CH}_{\text{cis}}$), 5.40 (1 H, dd, J 2 and 17.4, $\text{CCH}=\text{CH}_{\text{trans}}$), 6.18 (1 H, dd, J 10.9 and 17.4, $\text{CCH}=\text{CH}_2$) and 7.20–7.40 (5 H, m, aromatic); δ_{C} 151.2 (COCH_3), 141.20 (CCH_3), 129.43, 128.05, 127.21, 126.80, 118.42 (aromatic and alkenyl carbons), 113.32 ($\text{C}=\text{CH}_2$), 59.01 (OCH_3) and 18.09 (CCH_3); *3Z* isomer: δ_{H} 2.07 (3 H, s, CCH_3), 3.26 (3 H, s, OCH_3), 5.22 (1 H, dd, J 2.2 and 10.9, $\text{CCH}=\text{CH}_{\text{cis}}$), 5.54 (1 H, dd, J 2.2 and 17.2, $\text{CCH}=\text{CH}_{\text{trans}}$), 6.61 (1 H, dd, J 10.9 and 17.2, $\text{CCH}=\text{CH}_2$) and 7.21–7.40 (5 H, m, aromatic).

3-Methoxy-4-methylpenta-1,3-diene 12. Obtained as a colourless oil (45%) [Found: C, 75.2; H, 10.6%; ($M + \text{H}$) $^+$, 113.0966]. $\text{C}_7\text{H}_{12}\text{O}$ requires C, 74.94; H, 10.79%; $M + \text{H}$, 113.0966; δ_{H} 2.75, 2.83 (2 × 3 H, 2 × br s, 2 × CH_3), 3.53 (3 H, s, OCH_3), 5.02 (1 H, br d, J 9, $\text{CCH}=\text{CH}_{\text{cis}}$), 5.33 (1 H, br d, J 16, $\text{CCH}=\text{CH}_{\text{trans}}$) and 6.43 (1 H, dd, J 9 and 16, $\text{CCH}=\text{CH}_2$); δ_{C} 162.23 (COCH_3), 149.46 (CMe_2), 127.78 ($\text{CCH}=\text{CH}_2$), 112.11 ($\text{C}=\text{CH}_2$), 58.84 (COCH_3) and 18.34, 17.89 (2 × CH_3).

3-Methoxy-4-(4'-methoxyphenyl)-2-methylbuta-1,3-diene 13. Obtained as a pale yellow oil (74%) which was a 2:1 mixture of *3E* and *3Z* isomers (Found: M^+ , 204.1180). $\text{C}_{13}\text{H}_{16}\text{O}_2$ requires M , 204.1150). *3E* isomer: δ_{H} 1.83 (3 H, s, CCH_3), 3.64 (3 H, s, COCH_3), 3.75 (3 H, s, ArOCH_3), 5.10 (2 H, m, $\text{C}=\text{CH}_2$), 5.91 (1 H, s, ArCH) and 6.74 and 7.16 (2 × 2 H, 2 × d, J 8.9, aromatic); δ_{C} 157.53 (ArCOCH_3), 157.35 (COCH_3), 140.43 (CCH_3), 128.60 (ArCH), 139.31, 128.15, 118.48 (aromatic carbons), 113.61 ($\text{C}=\text{CH}_2$), 55.40 (ArOCH_3), 54.94 (COCH_3) and 20.89 (CH_3); *3Z* isomer: δ_{H} 1.94 (3 H, s, CCH_3), 3.57 (3 H, s, COCH_3), 3.79 (3 H, s, ArOCH_3), 5.03 (1 H, br s, $\text{C}=\text{CH}$), 5.37 (1 H, br s, $\text{C}=\text{CH}$), 5.55 (1 H, s, ArCH) and 6.86 and 7.59 (2 × 2 H, 2 × d, J 8.9, aromatic).

3-Methoxy-2-methyl-4-phenylpenta-1,3-diene 14. Obtained as a pale yellow oil (67%) which was a >10:1 mixture of *3E* and *3Z* isomers. The *3E* isomer on purification by preparative TLC [alumina, 10% diethyl ether in light petroleum (bp 40–60 °C)] was obtained as a colourless oil (Found: C, 82.7; H, 8.9.

$\text{C}_{13}\text{H}_{16}\text{O}$ requires C, 82.92; H, 8.57%); δ_{H} 1.66 (3 H, br s, $\text{CH}_2=\text{CCH}_3$), 2.04 (3 H, s, ArCCH_3), 3.48 (3 H, s, COCH_3), 4.84 (1 H, br s, $\text{C}=\text{CH}$), 4.97 (1 H, br s, $\text{C}=\text{CH}$) and 7.10–7.75 (5 H, m, aromatic); δ_{C} 152.77 (COCH_3), 142.69 (ArCCH_3), 138.69, 137.83, 128.64, 126.44, 122.04 (aromatic and alkenyl carbons), 119.72 ($\text{C}=\text{CH}_2$), 56.33 (COCH_3) and 21.77 and 17.95 (2 × CH_3).

4-Methoxy-5-(4'-methoxyphenyl)penta-2,4-diene 15. Obtained as a pale yellow oil (65%) which was a 2:1 mixture of *2E,4E* and *2E,4Z* isomers (Found: M^+ , 204.1149, $\text{C}_{13}\text{H}_{16}\text{O}_2$ requires M , 204.1150). *2E,4E* isomer: δ_{H} 1.83 (3 H, dd, J 5, CCH_3), 3.58 (3 H, s, COCH_3), 3.69 (3 H, s, ArOCH_3), 5.49 (1 H, m, $\text{C}=\text{CHCH}_3$), 5.74 (1 H, m, $\text{CH}=\text{CHCH}_3$), 6.07 (1 H, s, ArCH) and 6.50–7.30 (4 H, m, aromatic); δ_{C} 157.32 (ArCOCH_3), 153.01 (COCH_3), 129.90, 128.89, 127.12, 123.68, 113.14, 100.78 (aromatic and alkenyl carbons), 54.40 (ArOCH_3), 53.98 (COCH_3) and 17.61 (CCH_3); *2E,4Z* isomer: δ_{H} 1.79 (3 H, dd, J 5, CCH_3), 3.53 (3 H, s, COCH_3), 3.67 (3 H, s, ArOCH_3), 5.47 (1 H, m, $\text{C}=\text{CHCH}_3$), 5.76 (1 H, m, $\text{CH}=\text{CHCH}_3$), 6.03 (1 H, s, ArCH) and 6.50–7.30 (4 H, m, aromatic).

4-Methoxynona-2,4-diene 16. Obtained as a pale yellow oil (81%) which was a 3:2 mixture of *2E,4E* and *2E,4Z* isomers (Found: M^+ , 154.1377). $\text{C}_{10}\text{H}_{18}\text{O}$ requires M , 154.1388). *2E,4E* isomer: δ_{H} 0.90 (3 H, m, CH_2CH_3), 1.30–1.50 (4 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.79 (3 H, d, J 5, $\text{CH}=\text{CHCH}_3$), 2.12 (2 H, m, $\text{CH}_2\text{CH}=\text{}$), 3.56 (3 H, s, OCH_3), 4.52 (1 H, t, J 7.5, $\text{CH}_2\text{CH}=\text{}$), 5.74 (1 H, br d, J 16, $\text{CH}=\text{CHCH}_3$) and 6.08 (1 H, d, J 16, $\text{CH}=\text{CHCH}_3$); δ_{C} 151.41 (COCH_3), 124.83, 122.23, 116.05 (alkenyl carbons), 53.36 (COCH_3), 32.66, 25.11, 21.64 (3 × CH_2), 17.44 ($\text{C}=\text{CCH}_3$) and 12.88 (CH_2CH_3).

4-Methoxy-5-phenylhexa-2,4-diene 17. Obtained as a pale yellow oil (72%) which was a 20:1 mixture of *2E,4E* and *2E,4Z* isomers. The *2E,4E* isomer, on purification by preparative TLC [alumina, 10% diethyl ether in light petroleum (bp 40–60 °C)] was obtained as a colourless oil (Found: C, 82.7; H, 8.3%; M^+ , 188.1184). $\text{C}_{13}\text{H}_{16}\text{O}$ requires C, 82.92; H, 8.57%; M , 188.1201); δ_{H} 1.69 (3 H, d, J 5.1, CHCH_3), 2.07 (3 H, s, CCH_3), 3.62 (3 H, s, COCH_3), 5.88 (1 H, dd, J 6.9 and 15.2, $\text{CH}=\text{CHCH}_3$), 6.05 (1 H, dd, J 1.4 and 15.2, $\text{CH}=\text{CHCH}_3$) and 7.05–7.40 (5 H, m, aromatic); δ_{C} 152.10 (COCH_3), 142.51 (ArC), 128.91, 128.28, 127.80, 126.46, 125.32, 123.89 (aromatic and alkenyl carbons), 58.98 (COCH_3) and 18.31 and 17.98 (2 × CH_3).

3-Methoxy-4-(4'-methoxyphenyl)-1-phenylbuta-1,3-diene 18. Obtained as a pale yellow solid (87%) which was a 3:1 mixture of *1E,3E* and *1E,3Z* isomers. The *1E,3E* isomer, on purification by preparative TLC [alumina, 10% diethyl ether in light petroleum (bp 40–60 °C)] was obtained as an off-white solid, mp 62–63 °C (from diethyl ether–petroleum) (Found: C, 81.0; H, 6.7%; M^+ , 266.1293). $\text{C}_{18}\text{H}_{18}\text{O}_2$ requires C, 81.16; H, 6.82%; M , 266.1301); δ_{H} 3.77 (3 H, s, COCH_3), 3.80 (3 H, s, ArOCH_3), 5.87 (1 H, s, ArCH), 6.24 (1 H, d, J 15.8, $\text{CH}=\text{CHPh}$), 6.58 (1 H, d, J 15.8, $\text{CH}=\text{CHPh}$) and 6.62–7.60 (4 H, m, aromatic); δ_{C} 161.6 (ArCOCH_3), 157.5 (COCH_3), 140.2, 140.1, 133.4–120.1, 116.3, 106.7 (aromatic and alkenyl carbons), 60.9 (ArOCH_3) and 57.6 (COCH_3).

3-Methoxy-1-phenylocta-1,3-diene 19. Obtained as a colourless oil (68%) which was a 3:1 mixture of *1E,3E* and *1E,3Z* isomers (Found: C, 83.4; H, 9.2%; M^+ 216.1515). $\text{C}_{15}\text{H}_{20}\text{O}$ requires C, 83.27; H, 9.33%; M , 216.1514). *1E,3E* isomer: δ_{H} 0.88 (3 H, m, CH_3), 1.20–1.60 (4 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.22 (2 H, m, $\text{CH}_2\text{CH}=\text{}$), 3.59 (3 H, s, OCH_3), 5.11 (1 H, t, J 8, $\text{CH}_2\text{CH}=\text{}$), 6.42 (1 H, d, J 15, $\text{CH}=\text{CHPh}$), 6.70 (1 H, d, J 15, $\text{CH}=\text{CHPh}$) and 7.10–7.45 (5 H, m, aromatic); δ_{C} 151.88 (COCH_3), 137.23, 128.41, 128.06, 127.15, 126.27, 119.75, 103.77 (aromatic and alkenyl carbons), 54.30 (OCH_3), 32.99, 25.86, 22.37 (3 × CH_2) and 13.87 (CH_3); *1E,3Z* isomer: δ_{H} 0.91 (3 H, m, CH_3), 1.19–1.56 (4 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.26 (2 H, m, $\text{CH}_2\text{C}=\text{}$), 3.62 (3 H, s, OCH_3), 4.75 (1 H, t, J 8, $\text{CH}_2\text{C}=\text{}$), 6.46

† To aid discussion of the stereochemistry of products 10–22 the structures have been numbered throughout the Experimental section from the carbon adjacent to R^2 except in cases where $\text{R}^2 = \text{Me}$ when the numbering begins from the methyl.

(1 H, d, *J* 15, CH=CHPh), 6.80 (1 H, d, *J* 15, CH=CHPh) and 7.16–7.48 (5 H, m, aromatic).

3-Methoxy-1,4-diphenylpenta-1,3-diene 20. Obtained as a pale yellow oil (94%) which was a > 10:1 mixture of 1*E*,3*E* and 1*E*,3*Z* isomers. The 1*E*,3*E* isomer, on purification by preparative TLC [alumina, 10% diethyl ether in light petroleum (bp 40–60 °C)] was obtained as a colourless oil (Found: C, 86.6; H, 7.1%; M⁺, 250.1359. C₁₈H₁₈O requires C, 86.35; H, 7.25%; M, 250.1358); δ_H 2.16 (3 H, s, CH₃), 3.71 (3 H, s, OCH₃), 6.63 (1 H, d, *J* 15.2, CH=CHPh), 6.81 (1 H, d, *J* 15.2, CH=CHPh) and 7.05–7.90 (10 H, m, aromatic); δ_C 151.15 (COCH₃), 140.98 (ArCCH₃), 136.99, 132.71, 128.97–126.34 (aromatic and alkenyl carbons), 58.86 (COCH₃) and 17.84 (CH₃).

3-Methoxy-4-methyl-1-phenylpenta-1,3-diene 21. Obtained as a pale yellow oil (82%) (Found: M⁺, 188.1202. C₁₃H₁₆O requires M, 188.1201); δ_H 1.83 (3 H, s, CH₃), 1.84 (3 H, s, CH₃), 3.64 (3 H, s, OCH₃), 6.68 (1 H, d, *J* 14, CH=CHPh), 6.97 (1 H, d, *J* 14, CH=CHPh) and 7.20–7.65 (5 H, m, aromatic); δ_C 149.01 (COCH₃), 137.51 [(CH₃)₂C], 128.38, 128.09, 127.23, 126.51, 123.22, 119.58 (aromatic and alkenyl carbons), 58.39 (COCH₃) and 18.62 and 18.19 (2 × CH₃).

3-Methoxy-1,4,4-triphenylbuta-1,3-diene 22. Obtained as a pale yellow solid (90%), mp 73–75 °C (from diethyl ether–petroleum) (Found: C, 88.1; H, 6.2%; M⁺, 312.1522. C₂₃H₂₀O requires C, 88.42; H, 6.46%; M, 312.1514); δ_H 3.70 (3 H, s, OCH₃), 6.73 (1 H, d, *J* 14, CH=CHPh), 7.01 (1 H, d, *J* 14, CH=CHPh) and 7.18–7.80 (15 H, m, aromatic); δ_C 153.26 (COCH₃), 140.77 (CPh₂), 137.13, 132.39–126.77, 123.44 (aromatic and alkenyl carbons) and 59.87 (COCH₃).

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