A Convenient One-pot Synthesis of 4-Methoxyalka-2,4-dienoates

Ewan F. Birse, Michael D. Ironside, Leslie McQuire, and Alistair W. Murray*
Department of Chemistry, University of Dundee, Dundee DD1 4HN, Scotland

4-Methoxyalka-2,4-dienoates, bearing a variety of substituents, have been conveniently prepared in a one-pot, double quenching reaction of ylides derived from α-methoxyallyl(diphenyl)phosphine oxides. The dienes are useful precursors of γ-keto-α,β-unsaturated esters.

Previous studies[1] have shown that α-methoxyallylphosphine oxides (**1a–c**) readily available from chlorodiphenylphosphine and acetals of α,β-unsaturated aldehydes,[2] form anions (**2a–c**) which react with various electrophiles to afford γ-adducts (**3**), which are related to phosphonic acid derivatives recently developed as homoenolate equivalents.[3] More recently,[4] it has been pointed out that the lithium anions of α-methoxyallylphosphine oxides containing bulky substituents at the terminal position of the allylic system, viz (**2d**), react with carbonyl compounds at the α-position to yield 2-methoxy-1,3-dienes (**6**) as mixtures of geometric isomers. A further general method employing the formation of the titanium ate complex (**4**) has been described[5] for directing the condensation of α-methoxyallylphosphine oxide anions with aldehydes at the α-position of the allyl system. Subsequent Horner–Wittig chemistry[6] of the resulting diastereoisomeric alcohols (**5**) provided an efficient and convenient synthesis of conjugated methoxy dienes of defined geometry. These latter reactions have established the operational equivalence between α-methoxyallylphosphine oxides and vinylacyl anion equivalents (**7**) (see Scheme 1).

The generally high yields, regioselectivity and stereoselectivity in these quenching reactions studied to date, together with the significantly different conditions which lead to γ- or to α-attack, suggest that double quenching sequences should have great synthetic potential. In particular, it seems reasonable to envisage a sequence of γ-attack followed by α-attack on the new anion (or ate complex), leading ultimately to the insertion of the methoxyallyl unit of the original phosphine oxide, between two electrophilic entities, see (**8**). If E² = R³CHO, the sequence then allows us to prepare a variety of methoxy dienes (**9**).

In this paper, we exploit such a procedure for the synthesis of 4-methoxyalka-2,4-dienoates (**9**; E¹ = CO₂R⁴), which are difficult to prepare by current methods. These in turn are readily hydrolysed to γ-oxo-α,β-unsaturated esters (**10**; E¹ = CO₂R⁴) which are important structural features of many natural products.[7]

Results and Discussion

α-Methoxyallyl(diphenyl)phosphine oxides (**1a–d**) were prepared in a one-pot sequence from chlorodiphenylphosphine and the dimethyl acetal of the appropriate α,β-unsaturated aldehyde. Preparative details, and spectroscopic evidence for the structure assignments for these phosphine oxides have been presented elsewhere.[4] The corresponding anions (**2**) were formed readily from these oxides by their treatment with either butyl-lithium or with lithium di-isopropylamide.

With dry carbon dioxide, lithium anions (**2a–c**), formed by treatment with butyl-lithium (1.1 equiv., −78 °C), reacted regiospecifically to provide the γ-adducts (**3**; E¹ = CO₂H) as the E isomers, thus confirming the trend observed in earlier work.[1] Phosphine oxide anion (**2d**) did not yield the correspond-

	R¹	R²
a;	H	H
b;	H	Me
c;	Me	H
d;	H	Ph
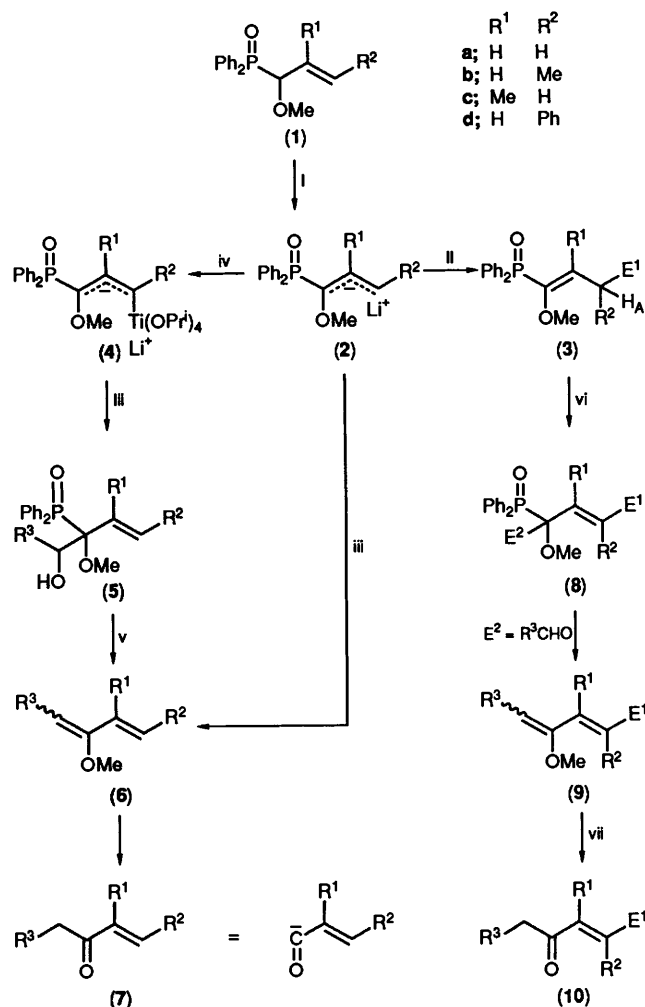
Scheme 1. *Reagents:* i, BuLi or LDA; ii, E′⁺; iii, R³CHO; iv, Ti(OPrⁱ)₄; v, KOBuᵗ in THF; vi, LDA, E²⁺; vii, Me₃SiCl,NaI,MeCN.

ing acid, presumably because steric factors prevented attack at the γ-position of this system.

The products were assigned as γ-adducts on the basis of their ¹H and ¹³C NMR spectra. Typically, the starting allylphosphine oxides (**1**) displayed a signal in their ¹H NMR at δ 3.25 for the methoxy protons, while in the products (**3**; E′ = CO₂H) these protons appeared at δ 3.4, or further downfield, characteristic of the transition from an ether to an enol ether.[8] Specifically, the starting allylphosphine oxide (**1b**) displayed in its ¹H NMR spectrum the methyl group as a double doublet at δ 1.69, ⁵J_{PH} 6 Hz, which in the product (**3b**) moved to a doublet at δ 1.29 with

no observable long-range phosphorus coupling.[9] In the ^{13}C NMR spectrum, the α-carbon of the allylic system resonated at δ 90 with J_{PC} 90 Hz, while in the product the same carbon atom appeared at δ 155 with J_{PC} 123 Hz. Further evidence for these assignments came from the observed phosphorus–hydrogen coupling constants. The coupling constants J_{PH} 8.5 and 10 Hz in (3a; E[1] = CO_2H) and (3b; E[1] = CO_2H), respectively, were indicative of a hydrogen atom Z to the phosphorus entity,[10] thus designating the products as the E isomers.

Acids (3a–c; E[1] = CO_2H) were readily esterified by adding thionyl chloride to a solution of the carboxylic acid in anhydrous methanol at −20 °C and subsequently warming to room temperature. On the other hand, the methyl esters (3; E[1] = CO_2Me) were prepared more conveniently by treating the appropriate allyl(diphenyl)phosphine oxide with 2.2 equiv. of LDA and quenching the resulting anion with methyl chloroformate. Use of 1 equiv. of base gave poor yields of adducts and much recovered isomerised starting material (11), presumably by transfer of the acidic proton, H_A in (3; E[1] = CO_2Me), to the lithium derivative (2) during the reaction. The presence of 2.2 equiv. of base gave good yields of esters.

The corresponding ethyl, allyl, and isopropyl esters were prepared in a similar manner by using the appropriate chloro-formate. Thus, isopropyl ester (12) was prepared as a 2:1 mixture of its E and Z isomers by replacing methyl chloroformate with isopropyl chloroformate.

Using this general procedure, (3a; E[1] = CO_2Me) was obtained as a single product in 83% yield, identical in all respects with the product of esterification of (3a; E[1] = CO_2H). Extending the methyl chloroformate procedure to (1b) gave an

(11) E - (12) Z - (12)

(13) (14)
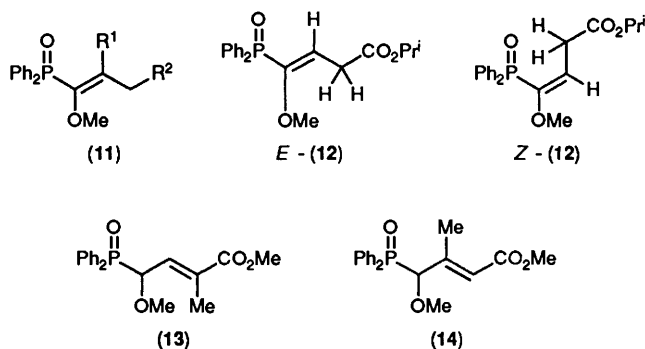
85% yield of a 1:1 mixture of the β,γ-unsaturated ester (3b; E[1] = CO_2Me) and its α,β-unsaturated isomer (13), while, under similar conditions, (1c) gave in 80% overall yield, the products (Z)-(3c; E[1] = CO_2Me), (E)-(3c; E[1] = CO_2Me), and (14) in a ratio of 1:2.3:9.

The structures of all these products were assigned on the basis of spectral evidence. The β,γ-unsaturated esters showed peaks at 1 720–1 730 cm⁻¹ in the IR region, while their α,β-unsaturated isomers displayed carbonyl absorption at 1 705 cm⁻¹. The general pattern of the ^{13}C and ^{1}H NMR spectra of the β,γ-unsaturated esters was comparable to that of the spectra of the previously obtained acids, while the spectra of each of the α,β-unsaturated esters was comparable to the spectra of the initial allylic phosphine oxides. The assignment of double bond stereochemistry of the esters was made primarily on the basis of the observed coupling constants. The premise was made[10] that in unsaturated phosphonic acids, $^3J_{PH}$ is 10–20 Hz for a hydrogen atom Z to the phosphorus entity, whereas $^3J_{PH}$ is 30–50 Hz for a hydrogen atom E to the phosphorus atom. This was confirmed by the observed coupling constants, $^3J_{PH}$ 9 Hz, and $^3J_{PH}$ 27.52 in (E)-(12) and (Z)-(12), respectively. The stereo-chemistry of (E)-(3b; E′ = CO_2Me) and (Z)-(3b; E′ = CO_2Me) was also assigned on the basis of a comparison with (E)-(12)

and (Z)-(12). Thus the methylene protons in (E)-(3c; E′ = CO_2Me) and (Z)-(3c; E′ = CO_2Me) appear at δ 3.37 and 3.64 respectively, in comparison with values δ 3.30 and 3.87 for similar protons in (E)-(12) and (Z)-(12). The fact that the methyl group in (E)-(3c; E′ = CO_2Me) resonates at δ 2.12 and that of (Z)-(3c; E′ = CO_2Me) at δ 1.94 lends support to these assignments. Such observations are not unexpected, since one would expect methylene and methyl protons Z to the di-phenylphosphinoyl moiety to be deshielded relative to those in the E configuration. Finally, the stereochemistries of both (13) and (14) were assigned as E on the basis of the coupling constants (J 1.4 Hz) observed between the vinyl methyl group and the E hydrogen atom in these compounds. The absorption at ca. δ 2 for the vinyl methyl in both these compounds was particularly significant as it is in accord with that for E stereochemistry.[11]

Earlier studies[4,5] on the reaction of α-methoxyallylphosphine oxide anions with carbonyl compounds have shown that either the use of the titanium ate complex, or the presence of large γ-substituents in the allylic system, normally ensures reaction of the anion at the α-position. In the present study this trend has been confirmed, and treatment of the 'ester mixture' with base [NaH with the parent ester (3a; E′ = CO_2Me), KH with the allylic esters, and LDA with the remainder] and then with an aldehyde, yielded 4-methoxyalka-2,4-dienoates (15–38) in good yields. Where it is possible for E and Z geometry to exist at the 4-position of these methoxy dienes, both isomers were usually observed, although E geometry predominated for both arom-atic and for aliphatic aldehydes. The formation of two geometric isomers is quite standard in Wittig–Horner reactions leading to enol ethers.[9,12] Unchanged aldehyde was removed as its bisulphite derivative.

The isomers were distinguished by their ^{1}H NMR spectra, and in particular from difference NOE experiments (see Figure).
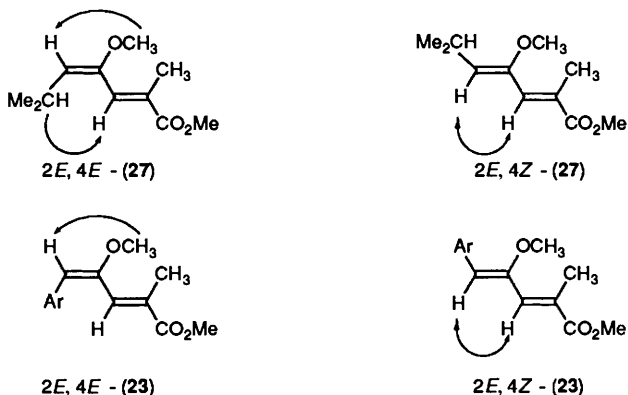

Figure. Enhancements are obtained for those nuclei at the arrow heads on irradiating those at the arrow-tails.

Thus, in the product (27) obtained from reaction of the mixture of (3b; E′ = CO_2Me) and (13) with base and isobutyraldehyde, irradiation of the signal at δ 2.60 (6-H) in the major isomer (slower moving by TLC) showed an NOE enhancement at 3-H, while in the minor isomer, no effect was observed at 3-H upon irradiation of 6-H. The major isomer also showed enhancement of the vinylic hydrogen at C-5 when the methoxy signal was irradiated, whereas only in the minor isomer did the vinylic hydrogen atoms at C-3 and C-5 display mutual NOE en-hancements. These effects define the stereochemistry of (4E)-(27) and (4Z)-(27) unambiguously, and establish that the major isomer is the 4E isomer. Similar effects were observed for the diene esters, (23), (28), (29), and (31) and the stereochemistry of the 4,5-double bond in the other products was assigned by analogy. The stereochemistry about the 2,3-double bond was

Table 1. 4-Methoxyalka-2,4-dienoates from γ-methoxyallyl(diphenyl)phosphine oxides.
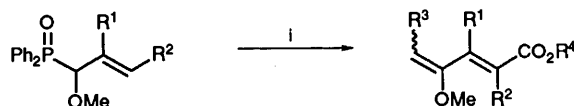
Reagents: i, 2.2 equiv. LDA, 1 equiv. $ClCO_2R^4$, 1 equiv. R^3CHO added in sequence.

			1,3-Diene		
Phosphine oxide	R^4	R^3	Product	Yield (%)[a]	4E–4Z[b]
(1a)	Me	C_6H_5	(15)	65	3:1
	Me	p-$MeOC_6H_4$	(16)	52	5:1
	Me	o-allyloxyphenyl	(17)	73	2:1
	Et	p-MeC_6H_4	(18)	62	3:1
	Et	o-but-2-enyloxyphenyl	(19)	62	3:2
	Et	o-prop-2-ynyloxyphenyl	(20)	72	3:2
	Et	Me_2CH	(21)	45	>10:1
	allyl	p-$MeOC_6H_4$	(22)	45	3:2
(1b)	Me	p-$MeOC_6H_4$	(23)	80	2:1
	Me	o-$MeOC_6H_4$	(24)	72	3:2
	Me	o-allyloxyphenyl	(25)	83	5:4
	Me	C_6H_{11}	(26)	48	3:1
	Me	Me_2CH	(27)	27	3:1
	Me	$Me[CH_2]_3$	(28)	59	3:1
	Me	$Me[CH_2]_8$	(29)	57	4:1
	Et	p-$MeOC_6H_4$	(30)	72	3:1
	Et	p-MeC_6H_4	(31)	70	4:1
	Et	o-prop-2-ynyloxyphenyl	(32)	74	5:1
	Et	H	(33)	58	—
	Et	Me	(34)	58	5:3
	Et	$MeCH_2$	(35)	60	2:1
	Et	Me_2CH	(36)	63	5:2
	allyl	p-$MeOC_6H_4$	(37)	55	2:1
(1c)	Et	o-allyloxyphenyl	(38)	55	>10:1

[a] Yields quoted are for isolated product from the one-pot reaction. [b] Estimated from the ratio of the integrals (in the NMR) for the methoxy protons and/or the protons on the 5-position.

assigned as E in every case from the observed $^3J_{HH}$ (15 Hz) and $^4J_{HH}$ (1.4 Hz) coupling constants.

(39)   (40)
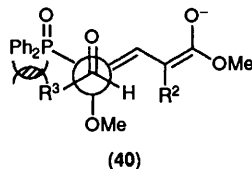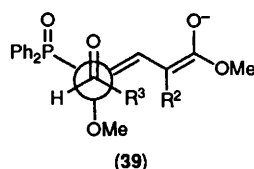
Any attempt to account for the formation of E isomers in preference to Z isomers in these reactions will always be open to debate. However, a tentative explanation of the observed facts can be made by postulating the involvement of transition states (39) or (40) in which the anion is considered to exist as an extended enolate. It would then appear that the unfavourable steric interaction between the diphenylphosphinoyl moiety and the alkyl or aryl group of the aldehyde would tend to favour (39) over (40), leading to the observed product distribution. A similar model has been predicted to account for the diastereoselectivity in reactions of prochiral carbanions with prochiral carbonyl compounds in the absence of chelate control.[13]

In view of the success of the step-wise double-quenching procedure described above, it was anticipated that treatment of the starting alkoxyallyl(diphenyl)phosphine oxides (1) with 2 equivalents of base, followed by addition of 1 equivalent of aldehyde, would provide access to 4-methoxyalka-2,4-dienoates

(9; $E' = CO_2Me$) in a one-pot operation. Indeed, this was found to be the case, and using such a procedure, higher yields of dienes identical in all respects with those obtained earlier, were obtained (see Table 1).

It is normal for ylides derived from α-hetero substituted alkylphosphine oxides to yield intermediate β-hydroxyalkyl-phosphine oxides from carbonyl compounds,[14] and the isolation and separation of such diastereoisomers has provided a basis for stereospecific alkene synthesis.[12] In the present study, no such intermediates were observed, probably because the considerable conjugation possible in the diene–ester product favours the cyclo-elimination of phosphorus,[15] and the behaviour of oxides (3) is therefore analogous to that described for other γ-substituted allylic phosphine oxides.[16] The ease of the elimination step in the present synthesis of these 4-methoxyalkadienoates 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 can be hydrolysed to enones, as is the case with the current series of compounds which contain a latent carbonyl function, this will not be important.

As expected, dienol methyl ethers (9; $E' = CO_2Me$) proved to be useful precursors of 4-oxobutenoates (10; $E' = CO_2Me$) and a comparison of methods for their cleavage, showed that treatment with aqueous acid proved successful and gave acceptable yields of γ-keto α,β-unsaturated esters (41)–(45), see Table 2, while using trimethylsilyl iodide[17] was found to be less satisfactory.

Table 2. Synthesis of γ-keto-α,β-unsaturated esters.

	Starting material	Product (% yield)
	(23)	(41) (80)
	(24)	(42) (76)
	(27)	(43) (64)
	(28)	(44) (41)
	(29)	(45) (57)

Experimental

M.p.s 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 and those of solids as Nujol mulls. Mass spectra were determined with an AEI MS9 spectrometer. NMR spectra were recorded on Bruker AM300/WB(300 MHz) (for ^{1}H) and Bruker AM300/WB(75.5 MHz) (for ^{13}C) spectrometers. Unless otherwise stated, the samples were dissolved in $CDCl_3$ and the chemical shifts are expressed in ppm downfield from tetramethylsilane as internal standard. The assignments were established using Waltz decoupled ^{13}C spectra, DEPT-sequence spectra, high resolution ^{1}H spectra, ^{1}H NOE-difference spectra, and ^{1}H COSY spectra.

General Procedure for the Reaction of the Anions of α-Methoxyallyl(diphenyl)phosphine Oxides with Carbon Dioxide.—A solution of the appropriate phosphine oxide (10 mmol) in anhydrous THF (30 ml) in a flame-dried flask under a positive pressure of nitrogen was cooled to $-78\ ^\circ$C. Butyl-lithium (1.1 equiv.) in hexane was added slowly and the resulting red solution stirred at that temperature for 30 min. Dry carbon dioxide was bubbled slowly into the solution which rapidly turned yellow and some precipitate formed. Carbon dioxide addition was continued for a further 15 min, the solution was stirred for several hours at $-78\ ^\circ$C, and then allowed to warm slowly to room temperature before being quenched with saturated aqueous $NaHCO_3$ (50 ml). Inorganic material was removed by filtration and washed with CH_2Cl_2; the THF layer was evaporated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 ml). The organic layers were combined and back-extracted with saturated aqueous $NaHCO_3$ (2 × 20 ml). The combined aqueous layers were acidified with 3M HCl, saturated with NaCl, and extracted with CH_2Cl_2 (3 × 30 ml). The volume was reduced on a rotary evaporator and the solution dried (Na_2SO_4). Filtration and evaporation yielded the crude product.

(E)-4-*Diphenylphosphinoyl-4-methoxybut-3-enoic acid* (**3a**; E′ = CO_2H). Obtained as a white crystalline solid (74%), m.p. 132.5–134 °C (toluene–hexane), v_{max} 3 000–2 600 (OH), 1 729 (C=O), 1 435 (P–Ph), and 1 170 cm^{-1} (P=O); δ_H 3.3 (2 H, dd, J_{PH} 2.5 and J_{HH} 7 Hz, CH_2), 3.57 (3 H, s, PCOMe), 6.05 (1 H, m, J_{PH} 8.5 and J_{HH} 7 Hz, C=CH), 7.3–7.95 (10 H, m, 2 × Ph), and 10.9 (1 H, br s, CO_2H); δ_C 171.45 (CO), 152.72 (d, J_{PC} 123.6 Hz, PCOMe), 135.08, 132.11, 131.68, 131.01, 129.07, 123.75 (ArC), 121.66 (C=CH), 60.77 (OMe), and 31.14 (d, J_{PC} 11 Hz, CH_2) (Found: C, 64.6; H, 5.4; P, 9.8. $C_{17}H_{17}O_4P$ requires C, 64.54; H, 5.43; P, 9.79%).

(E)-4-*Diphenylphosphinoyl-4-methoxy-2-methylbut-3-enoic acid* (**3b**; E′ = CO_2H). Obtained as a white crystalline solid (69%), m.p. 88–90 °C (toluene–hexane), v_{max} 3 000–2 600 (OH), 1 720 (C=O), 1 435 (P–Ph), and 1 160 cm^{-1} (P=O); δ_H 1.29 (3 H,

d, J_{HH} 7 Hz, CHMe), 3.53 (3 H, s, PCOMe), 3.76 (1 H, m, CHMe), 5.98 (1 H, m, J_{PH} 10 and J_{HH} 10 Hz, C=CH), 7.37–7.93 (10 H, m, 2 × Ph), and 11.54 (1 H, s, CO_2H); δ_C 175.29 (CO), 154.77 (d, J_{PC} 123 Hz, PCOMe), 133.64, 133.46, 132.19, 129.04, 128.85, 128.12, 122.72 (ArC and C=CH), 61.46 (OMe), 37.36 (CHMe), and 17.44 (Me) (Found: C, 65.4; H, 5.6; P, 9.5. $C_{18}H_{19}O_4P$ requires C, 65.43; H, 5.80; P, 9.38%).

(E)-4-*Diphenylphosphinoyl-4-methoxy-3-methylbut-3-enoic acid* (**3c**; E′ = CO_2H). Obtained as a white crystalline solid (70%), m.p. 175–176 °C (toluene–hexane), v_{max} 3 000–2 600 (OH), 1 710 (C=O), 1 435 (P–Ph), and 1 165 cm^{-1} (P=O); δ_H 2.02 (3 H, d, J_{HH} 3 Hz, Me), 3.39 (2 H, s, CH_2), 3.59 (3 H, s, PCOMe), 7.38–8.1 (10 H, m, 2 × Ph), and 10.7 (1 H, s, CO_2H); δ_C 172.41 (CO), 146.50 (d, J_{PC} 125.6 Hz, PCOMe), 132.65, 132.47, 132.20, 131.98, 131.22, 131.66, 128.75 (ArC and C=CMe), 61.25 (OMe), 32.61 (CH_2), and 17.7 (Me) (Found: C, 65.5; H, 5.8; P, 9.4. $C_{18}H_{19}O_4P$ requires C, 65.43; H, 5.80; P, 9.38%).

General Procedure for Converting the Acids into their Methyl Esters.—The appropriate diphenylphosphinoylbutenoic acid (10 mmol) was dissolved in anhydrous methanol (75 ml), the solution cooled to $-20\ ^\circ$C, thionyl chloride (4 equiv.) slowly added, and the solution allowed to warm to room temperature. After the mixture had been stirred for a further 6 h, toluene was added and the solvent removed on the rotary evaporator. The residue was dissolved in CH_2Cl_2 (100 ml), the organic layer washed with saturated aqueous $NaHCO_3$ (3 × 50 ml), dried (Na_2SO_4), and the solvent removed to afford the corresponding methyl ester as a single isomer.

Methyl (E)-4-*diphenylphosphinoyl-4-methoxybut-3-enoate* (**3a**; E′ = CO_2Me). Obtained as a white crystalline solid (90%), m.p. 106–107 °C (toluene–hexane), v_{max} 1 720 (C=O), 1 435 (P–Ph), and 1 190 cm^{-1} (P=O); δ_H 3.29 (2 H, dd, J_{PH} 2 and J_{HH} 7.5 Hz, CH_2), 3.60 (3 H, s, PCOMe), 3.64 (3 H, s, CO_2Me), 5.9 (1 H, m, J_{PH} 9 and J_{HH} 7.5 Hz, C=CH), and 7.33–8.0 (10 H, m, 2 × Ph); δ_C 170.54 (CO), 153.78 (d, J_{PC} 119 Hz, PCOMe), 134.9, 133.68, 132.11, 130.53, 128.89, 123.24 (ArC), 121.30 (CHCOMe), 60.89 (PCOMe), 51.85 (CO_2Me), and 31.14 (d, J_{PC} 10.98 Hz, CH_2) (Found: C, 65.5; H, 5.9; P, 9.4. $C_{18}H_{19}O_4P$ requires C, 65.43; H, 5.80; P, 9.38%).

Methyl (E)-4-*diphenylphosphinoyl-4-methoxy-2-methylbut-3-enoate* (**3b**; E′ = CO_2Me). Obtained as a pale yellow oil (84%) which was purified by chromatography on silica gel (Et_2O–CH_2Cl_2, 1:1), v_{max} 1 735 (C=O), 1 435 (P–Ph), and 1 170 cm^{-1} (P=O); δ_H 1.28 (3 H, d, J_{HH} 6.7 Hz, CHMe), 3.5 (3 H, s, PCOMe), 3.58 (3 H, s, CO_2Me), 3.77 (1 H, m, J_{PH} 9 and J_{HH} 6.7 Hz, CHMe), 5.77 (1 H, t, J_{PH} 9 and J_{HH} 9 Hz, PCCH), and 7.2–8.0 (10 H, m, 2 × Ph) (Found: C, 66.3; H, 6.3; P, 9.1. $C_{19}H_{21}O_4P$ requires C, 66.26; H, 6.16; P, 8.99%).

Methyl (E)-4-*diphenylphosphinoyl-4-methoxy-3-methylbut-3-enoate* (**3c**; E′ = CO_2Me). Obtained as a white crystalline solid (78%), m.p. 110–111.5 °C (toluene–hexane), v_{max} 1 735 (C=O), 1 625 (C=C), 1 435 (P–Ph), and 1 165 cm^{-1} (P=O); δ_H 2.12 (3 H, d, J_{PH} 2.5 Hz, (C=CMe), 3.06 (3 H, s, CO_2Me), 3.37 (2 H, br s, CH_2), 3.68 (3 H, s, PCOMe), and 7.36–8.05 (10 H, m, 2 × Ph); δ_C 170.56 (CO), 147.86 (d, J_{PC} 124 Hz, PCOMe), 138.12, 137.81, 133.33, 132.18, 131.59, 128.31, 128.18 (ArC and C=CMe), 60.89 (PCOMe), 51.91 (CO_2Me), 38.04 (d, J_{PC} 8.5 Hz, CH_2), and 17.34 (Me) (Found: C, 66.4; H, 6.0; P, 9.1. $C_{19}H_{21}O_4P$ requires C, 66.26; H, 6.16; P, 8.99%).

General Procedure for Reaction of the Anions of α-Methoxyallyl(diphenyl)phosphine Oxides with Chloroformates.—The phosphine oxide (10 mmol) was dissolved in anhydrous THF (30 ml) and slowly added to a solution of LDA (2.2 equiv.) in THF (70 ml) at $-78\ ^\circ$C, and the mixture stirred for 30 min. The appropriate chloroformate (1.05 equiv.) in anhydrous THF (20 ml) was added over a period of 1 h to the anion mixture

which was kept at -78 °C. The resulting solution was stirred for several hours at that temperature, then allowed to warm slowly to room temperature before being quenched by pouring into saturated aqueous NH_4Cl. Inorganic material was filtered off and washed with CH_2Cl_2, the THF layer was evaporated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 ml). The combined organic extracts were washed with a saturated brine (30 ml), dried (Na_2SO_4), and the solvent removed to afford crude product which was separated by flash column chromatography on silica gel [Et_2O–CH_2Cl_2 (1:1) + 1% MeOH]. The products were finally purified by recrystallisation from toluene–hexane or by preparative TLC [Et_2O–CH_2Cl_2 (1:1)].

Methyl (E)-4-*diphenylphosphinoyl-4-methoxybut-3-enoate* (**3a**; E′ = CO_2Me). Obtained as a white solid (83%), identical in all respects with the compound prepared earlier by esterification of (*E*)-4-diphenylphosphinoyl-4-methoxybut-3-enoic acid.

Reaction of 1-*Diphenylphosphinoyl-1-methoxybut-2-ene with Methyl Chloroformate.*—The crude product (85%) obtained on work-up was a 1:1 mixture of *methyl* (E)-4-*diphenylphosphinoyl-4-methoxy-2-methylbut-2-enoate* (**13**) and *methyl* (E)-4-*diphenylphosphinoyl-4-methoxy-2-methylbut-3-enoate* (**3b**; E′ = CO_2Me). The 2*E* isomer crystallised from toluene–hexane, m.p. 152–154 °C; v_{max} 1 705 (C=O), 1 640 (C=C), 1 430 (P–Ph), and 1 132 cm^{-1} (P=O); δ_H 1.99 (3 H, dd, J_{PH} 3.6 and J_{HH} 1.4 Hz, CH=C*Me*), 3.27 (3 H, s, PCOMe), 3.71 (3 H, s, CO_2Me), 4.92 (1 H, dd, J_{PH} 12 and J_{HH} 9.4 Hz, CHOMe), 6.70 (1 H, m, J_{PH} 4.5 and J_{HH} 9.4 Hz, C*H*=CMe), and 7.33–8.15 (10 H, m, 2 × Ph); δ_C 167.16 (CO), 134.68 (C=*C*Me), 134.01, 132.09, 131.56, 130.89, 130.15, 128.85 (ArC), 128.36 (*C*H=C), 78.47 (d, J_{PC} 87 Hz, PCOMe), 58.27 (d, J_{PC} 11.9 Hz, PCO*Me*), 51.38 (CO_2Me), and 13.01 (C=*C*Me) (Found: C, 66.4; H, 6.1; P, 9.1. $C_{19}H_{21}O_4P$ requires C, 66.26; H, 6.16; P, 8.99%).

The mother liquor was purified as in the general procedure to afford the 3*E* isomer which was identical in all respects to that prepared previously.

Reaction of 1-*Diphenylphosphinoyl-1-methoxy-2-methylprop-2-ene with Methyl Chloroformate.*—The crude syrup was separated into three products:

Methyl (E)-4-*diphenylphosphinoyl-4-methoxy-3-methylbut-2-enoate* (**14**). Obtained as a white solid (58%), m.p. 137–139 °C; v_{max} 1 705 (C=O), 1 640, 1 583 (C=C), 1 430 (P–Ph), and 1 170 cm^{-1} (P=O); δ_H 2.25 (3 H, d, J_{HH} 1.4 Hz, C=CMe), 3.30 (3 H, s, PCOMe), 3.61 (3 H, s, CO_2Me), 4.43 (1 H, d, J_{PH} 13.5 Hz, PCHOMe), 5.78 (1 H, br s, C*H*CO$_2$Me), and 7.30–8.15 (10 H, m, 2 × Ph); δ_C 165.99 (CO), 151.55 (CH=*C*Me), 132.29, 131.85, 131.04, 128.99, 128.25, 127.80 (ArC), 117.86 (d, J_{PC} 8.5 Hz, *C*H–CMe), 85.93 (d, J_{PC} 83.3 Hz, PCHOMe), 55.86 (d, J_{PC} 11.9 Hz, PCO*Me*), 50.81 (CO_2Me), and 17.30 (C=*C*Me) (Found: C, 66.2; H, 6.0; P, 8.8. $C_{19}H_{21}O_4P$ requires C, 66.26; H, 6.16; P, 8.99%).

Methyl (E)-4-*diphenylphosphinoyl-4-methoxy-3-methylbut-3-enoate* (**3c**; E′ = CO_2Me). Obtained as a white solid (14.5%), m.p. 110–111.5 °C, identical in all respects to that prepared earlier.

Methyl (Z)-4-*diphenylphosphinoyl-4-methoxy-3-methylbut-3-enoate* (**3c**; E′ = CO_2Me). Obtained as a straw-coloured oil (6.5%); v_{max} 1 730 (C=O), and 1 435 cm^{-1} (P–Ph); δ_H 1.94 (3 H, d, J_{PH} 2.5 Hz, C=CMe), 3.02 (3 H, s, CO_2Me), 3.59 (3 H, s, PCOMe), 3.64 (2 H, br s, CH$_2$), and 7.30–8.10 (10 H, m, 2 × Ph) (Found: C, 66.5; H, 6.4; P, 9.2. $C_{19}H_{21}O_4$ requires C, 66.26; H, 6.16; P, 8.99%).

Reaction of 1-*Diphenylphosphinoyl-1-methoxyprop-2-ene with Isopropyl Chloroformate.*—The crude product (87%) obtained on work-up was a 4:3 mixture of *isopropyl* (E)-4-*diphenylphosphinoyl-4-methoxybut-3-enoate* E-(**12**) and *isopropyl* (Z)-4-*diphenylphosphinoyl-4-methoxybut-3-enoate* Z-(**12**). The E

isomer was obtained as a pale yellow oil, δ_H 1.22 (6 H, d, J_{HH} 6.5 Hz, CH*Me*$_2$), 3.30 (2 H, dd, J_{PH} 2 and J_{HH} 7 Hz, CH$_2$), 3.6 (3 H, s, OMe), 4.95 (1 H, m, J_{PH} 9 and J_{HH} 7 Hz, C*H*Me$_2$), 5.9 (1 H, m, CH=C), and 7.3–8.0 (10 H, m, 2 × Ph) (Found: C, 67.2; H, 6.6; P, 8.5. $C_{20}H_{23}O_4P$ requires C, 67.02; H, 6.48; P, 8.64%).

The Z isomer was also a pale yellow oil, δ_H 1.18 (6 H, d, J_{HH} 6 Hz, CH*Me*$_2$), 3.52 (3 H, s, OMe), 3.87 (2 H, dd, J_{PH} 2 and J_{HH} 7 Hz, CH$_2$), 4.97 (1 H, m, C*H*Me$_2$), 5.6 (1 H, dt, J_{PH} 27.5 and J_{HH} 7.2 Hz, C*H*=C), and 7.05–7.95 (10 H, m, 2 × Ph) (Found: C, 67.0; H, 6.5; P, 8.8. $C_{20}H_{23}O_4P$ requires C, 67.02; H, 6.48; P, 8.64%).

Reaction of 1-*Diphenylphosphinoyl-1-methoxyprop-2-ene with Allyl Chloroformate.*—*Allyl* (E)-4-*diphenylphosphinoyl-4-methoxybut-3-enoate* (**3a**; E′ = $CO_2CH_2CH=CH_2$) was isolated as a pale yellow oil (67%), v_{max} 1 725 (C=O), 1 645 (C=C), 1 435 (P–Ph), and 1 170 cm^{-1} (P=O); δ_H 3.36 (2 H, dd, J_{PH} 2 and J_{HH} 7 Hz, CH$_2$), 3.63 (3 H, s, OMe), 4.60 (2 H, d, J_{HH} 6.5 Hz, OCH$_2$), 5.13–5.42 (2 H, m, CH=C*H*$_2$), 5.71–6.09 (2 H, m, C*H*=CH$_2$ and PC=CH), and 7.40–8.08 (10 H, m, 2 × Ph); δ_C 169.41 (CO), 153.12 (d, J_{PC} 119.02 Hz, P–C), 131.34–127.33 (ArC and CH=CH$_2$), 121.50 (d, J_{PC} 31.13 Hz, PC=*C*H), 117.56 (CH=*C*H$_2$), 64.62 (OCH$_2$), 60.16 (d, J_{PC} 2.8 Hz, OMe), and 30.59 (d, J_{PC} 10.1 Hz, *C*H$_2$CO) (Found: C, 67.2; H, 5.7; P, 8.5. $C_{20}H_{21}O_4P$ requires C, 67.40; H, 5.95; P, 8.69%).

Reaction of 1-*Diphenylphosphinoyl-1-methoxybut-2-ene with Allyl Chloroformate.*—The crude product (88%) obtained on work-up was a 2:3 mixture of *allyl* (E)-4-*diphenylphosphinoyl-4-methoxy-2-methylbut-3-enoate* (**3b**; E′ = $CO_2CH_2CH=CH_2$) and *allyl* (E)-4-*diphenylphosphinoyl-4-methoxy-2-methylbut-2-enoate* (**13**; $CO_2CH_2CH=CH_2$ for CO_2Me). The 2*E* isomer crystallised from toluene–hexane to afford a white solid, m.p. 98–100 °C; v_{max} 1 705 (C=O), 1 640 (C=C), 1 430 (P–Ph), and 1 182 cm^{-1} (P=O); δ_H 1.91 (3 H, dd, J_{PH} 3.6 and J_{HH} 1.4 Hz), 3.36 (3 H, s, OMe), 3.88 (1 H, dd, J_{PH} 12 and J_{HH} 8.2 Hz, PCH), 4.62 (2 H, d, J_{HH} 5.8 Hz, OCH$_2$), 5.16–5.42 (3 H, m, CH=CH$_2$), 6.80 (1 H, m, C*H*=CMe), and 7.44–8.09 (10 H, m, 2 × Ph); δ_C 168.72 (CO), 135.04 (CH=*C*Me), 134.74–128.18 (ArC and 2 × *C*H=C), 117.95 (C=*C*H$_2$), 78.28 (d, J_{PC} 86.1 Hz, PC), 64.50 (OCH$_2$), 58.52 (d, J_{PC} 11.8 Hz, OMe), and 16.59 (Me) (Found: C, 68.2; H, 6.4; P, 8.5. $C_{21}H_{23}O_4P$ requires C, 68.09; H, 6.27; P, 8.36%).

The 3*E* isomer was obtained as a colourless oil, v_{max} 1 735 (C=O) 1 640 (C=C), 1 435 (P–Ph), and 1 170 cm^{-1} (P=O); δ_H 1.29 (3 H, d, J_{HH} 7 Hz, Me), 3.55 (1 H, m, C*H*Me), 3.64 (3 H, s, OMe), 4.62 (2 H, d, J_{HH} 5.8 Hz, OCH$_2$), 5.16–5.42 (3 H, m, CH=CH$_2$), 5.77–6.08 (1 H, m, PC=CH), and 7.44–8.09 (10 H, m, 2 × Ph); δ_C 165.98 (CO), 149.8 (d, J_{PC} 119.5 Hz, PC=C), 134.03–125.75 (ArC and *C*H=CH$_2$), 122.50 (d, J_{PC} 30.6 Hz, PC=*C*H), 116.95 (C=*C*H$_2$), 64.52 (OCH$_2$), 60.43 (OMe), 36.18 (d, J_{PC} 10 Hz, *C*HMe), and 12.83 (Me) (Found: C, 68.3; H, 6.5; P, 8.1. $C_{21}H_{23}O_4P$ requires C, 68.09; H, 6.27; P, 8.36%).

Reaction of 1-*Diphenylphosphinoyl-1-methoxy-2-methylprop-2-ene with Allyl Chloroformate.*—The crude syrup was separated into three products:

Allyl (E)-4-*diphenylphosphinoyl-4-methoxy-3-methylbut-2-enoate* (**14**; $CO_2CH_2CH=CH_2$ for CO_2Me), obtained as a pale yellow oil (35%), v_{max} 1 706 (C=O), 1 640, 1 583 (C=C), 1 430 (P–Ph), and 1 170 cm^{-1} (P=O); δ_H 2.26 (3 H, br s, Me), 3.29 (3 H, s, OMe), 4.54 (1 H, d, J_{PH} 13.5 Hz, PCH), 4.60 (2 H, d, J_{HH} 5.7 Hz, OCH$_2$), 5.16–5.53 (2 H, m, CHC*H*$_2$), 5.76 (1 H, br s, C*H*=CMe), 5.80–6.18 (1 H, m, C*H*=CH$_2$), and 7.32–8.05 (10 H, m, 2 × Ph); δ_C 166.23 (CO), 151.78 (CH=*C*Me), 135.28–127.53 (ArC and *C*H=CH$_2$), 118.34 (CH$_2$) 117.90 (d, J_{PC} 8.4 Hz, *C*H=CMe), 85.93 (d, J_{PC} 82.7 Hz, PCH), 64.04 (OCH$_2$), 58.65 (d, J_{PC} 11 Hz, OMe), and 17.30 (Me) (Found: C, 68.0; H, 6.1; P, 8.7. $C_{21}H_{23}O_4P$ requires C, 68.09; H, 6.27; P, 8.36%).

Allyl (E)-4-*diphenylphosphinoyl*-4-*methoxy*-3-*methylbut*-3-*enoate* (**3c**; E' = $CO_2CH_2CH=CH_2$), the slowest moving product was isolated as a pale yellow oil (10%), v_{max} 1 735 (C=O), 1 625 (C=C), 1 435 (P–Ph), and 1 165 cm⁻¹ (P=O); δ_H 2.11 (3 H, d, J_{PH} 2.5 Hz, Me), 3.37 (2 H, br s, CH_2CO), 3.56 (3 H, s, OMe), 4.58 (2 H, d, J_{HH} 5.9 Hz, OCH_2), 5.16–5.53 (2 H, m, CH=CH_2), 5.80–6.18 (1 H, m, CH=CH₂), and 7.32–8.05 (10 H, m, 2 × Ph) (Found: C, 67.9; H, 6.0; P, 8.5. $C_{21}H_{23}O_4P$ requires C, 68.09; H, 6.27; P, 8.36%).

Allyl (Z)-4-*diphenylphosphinoyl*-4-*methoxy*-3-*methylbut*-3-*enoate* (**3c**; E' = $CO_2CH_2CH=CH_2$), the least polar product was isolated as a yellow oil (5%), v_{max} 1 730 (C=O), 1 620 (C=C), 1 435 (P–Ph), and 1 165 cm⁻¹ (P=O); δ_H 1.93 (3 H, d, J_{PH} 2.5 Hz, Me), 3.53 (3 H, s, OMe), 3.65 (2 H, br s, CH_2CO), 4.65 (2 H, d, J_{HH} 5.8 Hz, OCH_2), 5.16–5.53 (2 H, m, CH=CH_2), 5.80–6.18 (1 H, m, CH=CH₂), and 7.32–8.05 (10 H, m, 2 × Ph) (Found: C, 68.0; H, 6.3; P, 8.6. $C_{21}H_{23}O_4P$ requires C, 68.09; H, 6.27; P, 8.36%).

General Procedures for the Preparation of Diene Esters.—(*a*) *Two-step procedure.* The phosphine oxide ester mixture (10 mmol), dissolved in anhydrous THF (30 ml), was stirred under nitrogen with NaH (1.2 equiv.) for 3 h at room temperature, after which time aldehyde (1 equiv.) was added. The mixture was stirred overnight and then quenched with saturated aqueous NH₄Cl (50 ml). The layers were separated and the THF layer was evaporated. The aqueous layer was extracted with ether (3 × 30 ml) and the combined extracts were washed with saturated aqueous NaHCO₃ and then with saturated brine and finally dried (MgSO₄). Subsequent filtration and evaporation afforded crude product. Residual aldehyde was removed as its bisulphite derivative by dissolving the crude diene ester in ether (50 ml) and stirring the solution with saturated aqueous NaHSO₃. The mixture was filtered, the layers separated, and the aqueous fraction extracted with ether; the combined organic layers were dried (MgSO₄), filtered, and evaporated. Flash-column chromatography of the residue on silica gel [Et₂O]–hexane (1:9)] afforded the diene esters as a mixture of 2E,4E and 2E,4Z isomers.

(*b*) *One-pot procedure.* The phosphine oxide (20 mmol) in anhydrous THF (20 ml) was added slowly to a solution of LDA (2 equiv.) in THF (30 ml) at −78 °C. The resultant dark-red solution of phosphine oxide anion was stirred at this temperature for 30 min prior to the dropwise addition of the appropriate chloroformate (1 equiv.) in anhydrous THF (20 ml). The reaction mixture was allowed to warm to 0 °C before the rapid addition of the aldehyde (1.1 equiv.) in THF (5 ml). The resulting solution was stirred at room temperature for 24 h before being quenched with water (50 ml). Ether (35 ml) was added, the layers were separated, and the organic portion was evaporated. The aqueous fraction was extracted with ether (3 × 25 ml), the organic portions were combined and washed sequentially with saturated aqueous NaHCO₃ (2 × 40 ml), and saturated brine (40 ml), and then dried (MgSO₄). Purification of the crude syrup by flash-column chromatography on silica gel [Et₂O–hexane (1:9)], afforded a mixture of the diene ester with traces of unchanged aldehyde. The latter was removed by dissolving the mixture in ether (50 ml) and stirring the solution with saturated aqueous NaHSO₃ for 48 h. The mixture was filtered and separated and the ether layer dried (MgSO₄), and evaporated. Flash chromatography of the residue [Et₂O–hexane (1:9) as eluant] gave the diene ester as a mixture of pure 2E,4E and 2E,4Z isomers. Samples of each

isomer were purified by preparative TLC⁻ [Et₂O–light petroleum (b.p. 40–60 °C) (1:19)].*

Procedure (*b*) proved to be the most efficient (see Table 1 for details).

Methyl 4-*methoxy*-5-*phenylpenta*-2,4-*dienoate* (**15**). 2E,4E Isomer, m.p. 77–79 °C (from diethyl ether–hexane) (Found: C, 71.5; H, 6.5%; M^+ 218.0936. $C_{13}H_{14}O_3$ requires C, 71.53; H, 6.47%; M, 218.0939); δ_H 3.67, 3.69 (2 × 3 H, 2 × s, OMe, CO_2Me), 6.10 (1 H, s, PhCH=), 6.35 (1 H, d, J 13.5 Hz, CH=$CHCO_2Me$), 7.11–7.38 (5 H, m, Ph), and 7.49 (1 H, d, J 13.5 Hz, CH=$CHCO_2Me$).

2E,4Z Isomer, colourless oil (Found: M^+, 218.093. $C_{13}H_{14}O_3$ requires M, 218.0939); δ_H 3.61 (3 H, s, OMe), 3.74 (3 H, s, CO_2Me), 6.14 (1 H, s, PhCH=), 6.16 (1 H, s, J 14 Hz, CH=$CHCO_2Me$), and 7.05–7.9 (6 H, m, Ph, CH=$CHCO_2Me$).

Methyl 4-*methoxy*-5-(4-*methoxyphenyl*)*penta*-2,4-*dienoate* (**16**). 2E,4E Isomer, m.p. 71.5–72.5 °C [from diethyl ether–light petroleum (b.p. 40–60 °C)] (Found: C, 67.8; H, 6.4%; M^+, 248.1048. $C_{14}H_{16}O_4$ requires C, 67.71; H, 6.50%; M, 248.1044); δ_H 3.68 (3 H, s, OMe), 3.70 (3 H, s, CO_2Me), 3.81 (3 H, s, ArOMe), 6.10 (1 H, br s, ArCH), 6.39 (1 H, d, J 15.5 Hz, CHCO₂Me), 6.93, 7.20 (2 × 2H, d, J 9 Hz, aromatic), and 7.53 (1 H, d, J 15.5 Hz, CH=$CHCO_2Me$); δ_C 168.50 (C=O), 158.72 (arene COMe) 150.98 (COMe), 144.86 (CH=$CHCO_2Me$), 134.12, 130.74, 113.74 (aromatic C) 129.92 (CH=$CHCO_2Me$), 110.19 (ArCH), 58.34 (ArOMe), 56.12 (OMe), and 51.43 (CO_2Me).

2E,4Z Isomer, colourless oil (Found: M^+, 248.1040. $C_{14}H_{16}O_4$ requires M, 248.1044); δ_H 3.64 (3 H, s, OMe), 3.78 (3 H, s, CO_2Me), 3.81 (3 H, s, ArOMe), 6.09 (1 H, br s, ArCH) 6.16 (1 H, d, J 16 Hz, CHCO₂Me), 6.75, 7.40 (2 × 2 H, d, J 9 Hz, aromatic H), and 7.24 (1 H, d, J 16 Hz, CH=$CHCO_2Me$); δ_C 168.50 (C=O), 159.14 (arene COMe), 151.71 (COMe), 144.94 (CH=$CHCO_2Me$), 134.78, 130.46, 113.68 (aromatic C), 129.43 (CH=$CHCO_2Me$), 109.76 (ArCH), 58.29 (ArOMe), 56.08 (OMe), and 51.44 (CO_2Me).

Methyl 5-(2-*allyloxyphenyl*)-4-*methoxypenta*-2,4-*dienoate* (**17**). 2E,4E Isomer, colourless oil (Found: C, 70.1; H, 6.5%; M^+, 274.1215. $C_{16}H_{18}O_4$ requires C, 70.04; H, 6.62%; M, 274.1200); δ_H 3.73 (3 H, s, OMe), 3.77 (3 H, s, CO_2Me), 4.53 (2 H, d, J 4 Hz OCH₂), 5.18–5.53 (2 H, m, CH=CH_2), 5.87–6.33 (1 H, m, CH=CH₂), 6.29 (1 H, s, ArCH), 6.42 (1 H, d, J 15.8 Hz, CH=$CHCO_2Me$), 6.73–7.33 (4 H, m, aromatic H), and 7.58 (1 H, d, J 15.8 Hz, CH=$CHCO_2Me$); δ_C 168.55 (C=O), 153.98 (arene COCH₂), 151.68 (COMe), 139.78 (CH=$CHCO_2Me$), 131.10, 129.03, 127.15, 126.12, 116.88, 115.43 (aromatic C with CH=CH₂) 122.66 (CH=$CHCO_2Me$), 117.44 (C=CH_2), 109.60 (ArCH), 68.85 (OCH₂), 57.65 (CO_2Me), and 54.60 (OMe).

2E,4Z Isomer, colourless oil (Found: M^+, 274.1216. $C_{16}H_{18}O_4$ requires M, 274.1200); δ_H 3.57 (3 H, s, OMe), 3.77 (3 H, s, CO_2Me), 4.53 (2 H, d, J 4.1 Hz, OCH₂), 5.18–5.53 (2 H, m, CH=CH_2), 5.87–6.30 (1 H, m, CH=CH₂), 6.22 (1 H, d, J 15.8 Hz, CH=$CHCO_2Me$), 6.27 (1 H, s, ArCH), 6.73–7.32 (4 H, m, aromatic H), and 7.33 (1 H, d, J 15.8 Hz, CH=$CHCO_2Me$); δ_C 168.55 (C=O), 153.80 (arene COCH₂), 149.80 (COMe), 134.62 (CH=$CHCO_2Me$), 130.91, 129.00, 127.70, 126.12, 125.85, 115.07 (aromatic C and CH=CH₂), 121.38 (CH=$CHCO_2Me$), 118.45 (CCH₂), 104.14 (ArCH), 68.43 (OCH₂), 57.65 (CO_2Me), and 51.73 (OMe).

Ethyl 4-*methoxy*-5-(p-*tolyl*)*penta*-2,4-*dienoate* (**18**). Obtained as a pale yellow oil which was a 3:1 mixture of 2E,4E and 2E,4Z isomers (Found: C, 73.3; H, 3.2%; M^+, 246.1232. $C_{15}H_{18}O_3$ requires C, 73.13; H, 7.37%; M, 246.1251).

2E,4E Isomer; δ_H 1.23 (3 H, t, J 7 Hz, OCH₂Me), 2.33 (3 H, s, ArMe), 3.73 (3 H, s, OMe), 4.22 (2 H, q, J 7 Hz, OCH_2Me), 6.19 (1 H, s, ArCH), 6.48 (1 H, d, J 16 Hz, CH=$CHCO_2Et$), 7.20 (4 H, br s, aromatic H), and 7.64 (1 H, d, J 16 Hz, CH=CHCO₂Et); δ_C 166.37 (C=O), 153.01 (COMe), 141.11 (CH=CHCO₂Et), 131.21,

* In cases where the separate isomers were not purified their ratio was estimated from the ratio of the integrals (in the NMR spectra) for the methoxy protons and/or the protons on the 5-position.

128.97, 126.02, 120.85 (aromatic C), 119.56 (CH=CHCO$_2$Et), 109.85 (ArCH), 60.73 (OCH$_2$), 50.96 (OMe), 20.48 (ArMe), and 13.68 (OCH$_2Me$).

2E,4Z Isomer; δ_H 1.29 (3 H, t, J 7 Hz, OCH$_2Me$), 2.34 (3 H, s, ArMe), 3.64 (3 H, s, OMe), 4.28 (2 H, q, J 7 Hz, OCH_2Me), 6.17 (1 H, s, ArCH), 6.27 (1 H, d, J 16 Hz, CH=CHCO$_2$Et), 7.22 (4 H, br s, aromatic H), and 7.29 (1 H, d, J 16 Hz, CH=CHCO$_2$Et); δ_C 165.87 (C=O), 151.68 (COMe), 141.10 (CH=CHCO$_2$Et), 131.10, 128.73, 126.42, 120.55 (aromatic C), 117.30 (CH=CHCO$_2$Et), 109.83 (ArCH), 60.73 (OCH$_2$), 50.96 (OMe), 20.46 (ArMe), and 13.66 (OCH$_2Me$).

Ethyl 5-(2-but-2-enyloxyphenyl)-4-methoxypenta-2,4-dieno-ate (**19**). Obtained as a pale yellow syrup which was a 3:2 mixture of 2E,4E and 2E,4Z isomers (Found: C, 71.6; H, 7.3; M^+, 302.1521. C$_{18}$H$_{22}$O$_4$ requires C, 71.49; H, 7.34%; M, 302.1512).

2E,4E Isomer; δ_H 1.24 (3 H, t, J 7.3 Hz, OCH$_2Me$), 1.78 (3 H, dd, J 6.2 and 1.2 Hz, CH–CHMe), 3.60 (3 H, s, OMe), 4.09 (2 H, q, J 7.3 Hz, OCH_2Me), 4.31 (2 H, d, J 5.4 Hz, ArOCH_2), 5.50 (2 H, m, CH=CH), 6.04 (1 H, s, ArCH), 6.35 (1 H, d, J 16 Hz, CH=CHCO$_2$Et), and 6.65–7.42 (5 H, m, aromatic and CH=CHCO$_2$Et); δ_C 166.51 (C=O), 156.01 (arene COCH$_2$), 153.41 (COMe), 141.76 (CH=CHCO$_2$Et), 130.87, 129.49, 126.42, 125.72, 124.51, 111.61 (aromatic C and CH=CHMe), 120.35 (CH=CHCO$_2$Et), 117.08 (CH=CHMe), 106.28 (ArCH), 68.53 (ArOCH$_2$), 59.72 (OCH$_2$Me), 50.94 (OMe), 17.29 (CH=CHMe), and 13.79 (Me).

2E,4Z Isomer; δ_H 1.26 (3 H, t, J 7.3 Hz, OCH$_2Me$), 1.79 (3 H, dd, J 6.2 and 1.2 Hz, CH=CHMe), 3.46 (3 H, s, OMe), 4.11 (2 H, q, J 7.3 Hz, OCH_2Me), 4.34 (2 H, d, J 5.4 Hz, ArOCH_2), 5.52 (2 H, m, CH=CH), 6.01 (1 H, s, ArCH), 6.39 (1 H, d, J 16 Hz, CH=CHCO$_2$Et), and 6.60–7.32 (5 H, m, aromatic and CH=CHCO$_2$Et); δ_C 166.58 (C=O), 156.02 (arene COCH$_2$), 151.57 (COMe), 142.02 (CH=CHCO$_2$Et), 129.71, 129.57, 127.97, 125.91, 111.54 (aromatic C and CH=CHMe), 120.11 (CH=CHCO$_2$Et), 117.69 (CH=CHMe), 106.43 (ArCH), 68.55 (ArOCH$_2$), 59.73 (OCH$_2$Me), 50.95 (OMe), 17.30 (CH=CHMe), and 13.80 (Me).

Ethyl 4-methoxy-5-(2-prop-2-ynyloxyphenyl)penta-2,4-dieno-ate (**20**). Workup and purification afforded an oil (72%), identified as a mixture (3:2) of the 2E,4E and 2E,4Z isomers (Found: C, 71.5; H, 6.1; M^+, 286.1270. C$_{17}$H$_{18}$O$_4$ requires C, 71.30; H, 6.34%; M, 286.1200).

2E,4E Isomer; δ_H 1.26 (3 H, t, J 7.4 Hz, OCH$_2Me$), 2.52 (1 H, br s, C≡CH), 3.61 (3 H, s, OMe), 4.16 (2 H, q, J 7.4 Hz, OCH_2Me), 4.84 (2 H, d, J 2.8 Hz, OCH$_2$), 6.36 (1 H, d, J 16.6 Hz, CH=CHCO$_2$Et), 6.61 (1 H, s, ArCH), 6.95–7.22 (4 H, m, aromatic H), and 7.23 (1 H, d, J 16.6 Hz, CH=CHCO$_2$Et); δ_C 167.18 (C=O), 155.19 (arene COCH$_2$), 154.10 (COMe), 142.05 (CHCHCO$_2$Et), 136.88–112.19 (aromatic C and CHCHCO$_2$-Et), 106.06 (ArCH), 78.63 and 78.40 (C≡CH), 60.41 (ArOCH$_2$) 56.30 (OCH$_2$Me), 55.14 (OMe), and 14.33 (OCH$_2Me$).

2E,4Z Isomer; δ 1.30 (3 H, t, J 7.4 Hz, OCH$_2Me$), 2.51 (1 H, br s, C≡CH), 3.78 (3 H, s, OMe), 4.22 (2 H, q, J 7.4 Hz, OCH_2Me), 4.85 (2 H, d, J 2.8 Hz, OCH$_2$), 6.19 (1 H, d, J 16.7 Hz, CH=CHCO$_2$Et), 6.21 (1 H, s, ArCH), 6.97–7.25 (4 H, m, aromatic H), and 7.42 (1 H, d, J 16.7 Hz, CH=CHCO$_2$Et); δ_C 167.18 (C=O), 154.96 (arene COCH$_2$), 152.23 (COMe), 142.10 (CH=CHCO$_2$Et), 136.88–112.19 (aromatic C and CH=CH-CO$_2$Et), 106.16 (ArCH), 75.88, 75.73 (C≡CH), 60.20 (ArOCH$_2$), 56.20 (OCH$_2$Me), 58.75 (OMe), and 14.16 (OCH$_2Me$).

Ethyl (2E,4E)-4-methoxy-6-methylhepta-2,4-dienoate (**21**). Work-up and purification afforded the 2E,4E isomer as an oil (Found: C, 66.8; H, 9.0; M^+, 198.1191. C$_{11}$H$_{18}$O$_3$ requires C, 66.62; H, 9.16%; M, 198.1251); δ_H 1.04 (6 H, d, J Hz, CHMe_2), 1.23 (3 H, t, J 7.3 Hz, OCH$_2Me$), 2.78 (1 H, br m, CHMe$_2$), 3.58 (3 H, s, OMe), 4.20 (2 H, q, J 7.3 Hz, OCH_2Me), 4.84 (1 H, d, J 9.5 Hz, CH=COMe), 6.29 (1 H, d, J 15.5 Hz, CH=CHCO$_2$Et), and 7.58 (1 H, d, J 15.5 Hz, CH=CHCO$_2$Et); δ_C 167.81 (C=O), 149.71

(COMe), 135.57 (CH=CHCO$_2$Et), 118.87 (CH=CHCO$_2$Et), 118.14 (CH=COMe), 60.59 (OCH$_2$Me), 54.82 (OMe), 31.10 (CHMe_2), 24.59 (CHMe$_2$), and 14.39 (OCH$_2Me$).

Allyl 4-methoxy-5-(4-methoxyphenyl)penta-2,4-dienoate (**22**). Obtained as a pale yellow oil which was 3:2 mixture of the 2E,4E and 2E,4Z isomers (Found: C, 70.1; H, 6.6%; M^+, 274.1206. C$_{16}$H$_{18}$O$_4$ requires C, 70.04; H, 6.62%; M, 274.1200).

2E,4E Isomer; δ_H 3.78 (3 H, s, OMe), 3.86 (3 H, s, ArOMe), 4.71 (2 H, d, J 6.1, OCH$_2$), 5.20–5.51 (2 H, m, C=CH$_2$), 5.89–6.16 (1 H, m, CH=CH$_2$), 6.19 (1 H, s, ArCH), 6.47 (1 H, d, J 16 Hz, CH=CHCO$_2$), 6.98, 7.24 (2 × 2 H, d, J 9 Hz, aromatic H), and 7.62 (1 H, d, J 16 Hz, CH=CHCO$_2$); δ_C 166.77 (C=O), 158.82 (arene COMe), 151.84 (COMe), 135.43 (CH=CHCO$_2$), 134.87 (CH=CH$_2$), 128.04, 125.67, 114.02 (aromatic C), 123.06 (CH=CHCO$_2$), 119.42 (CH=CH$_2$), 110.56 (ArCH), 64.17 (OCH$_2$), and 56.28, 55.13 (2 × OMe).

2E,4Z Isomer; δ_H 3.76 (3 H, s, OMe), 3.86 (3 H, s, ArOMe), 4.70 (2 H, d, J 6 Hz, OCH$_2$), 5.20–5.48 (2 H, m, CH=CH_2), 5.89–6.17 (1 H, m, CH=CH$_2$), 6.17 (1 H, s, ArCH), 6.44 (1 H, d, J 16 Hz, CH=CHCO$_2$), 6.98, 7.24 (2 × 2 H, d, J 9 Hz, aromatic H), and 7.60 (1 H, d, J 16 Hz, CH=CHCO$_2$); δ_C 166.42 (C=O), 158.54 (arene COMe), 152.10 (COMe), 135.66 (CH=CHCO$_2$), 133.85 (CH=CH$_2$), 128.04, 125.66, 114.04 (aromatic C), 122.87 (CH=CHCO$_2$), 119.42 (CH=CH$_2$), 110.31 (ArCH), 64.20 (OCH$_2$), and 56.28, 55.12 (2 × OMe).

Methyl 4-methoxy-5-(4-methoxyphenyl)-2-methylpenta-2,4-dienoate (**23**). 2E,4E Isomer, colourless oil (Found: C, 68.8; H, 7.0%; M^+, 262.1200. C$_{15}$H$_{18}$O$_4$ requires C, 68.67; H, 6.92%; M, 262.1200); δ_H 2.12 (3 H, d, J 1.4 Hz, CHCMe), 3.70 (3 H, s, COMe), 3.73 (3 H, s, CO$_2Me$), 3.75 (3 H, s, ArOMe), 5.98 (1 H, s, ArCH), 6.85, 7.15 (2 × 2 H, d, J 9 Hz, aromatic H), and 7.3 (1 H, d, J 1.4 Hz, CH=CMe); δ_C 168.98 (C=O), 158.49 (arene COMe), 152.98 (COMe), 135.10 (CH=CMe), 131.52 (CH=CMe), 130.45, 128.71, 113.84 (aromatic C), 108.84 (ArCH), 55.01 (ArOMe), 54.73 (COMe), 51.86 (CO$_2Me$), and 14.57 (Me).

2E,4Z Isomer, colourless oil (Found: M^+, 262.1200. C$_{15}$H$_{18}$O$_4$ requires M, 262.1200); δ_H 2.10 (3 H, d, J 1.4 Hz, CH=CMe), 3.68 (3 H, s, COMe), 3.72 (3 H, s, CO$_2$Me), 3.75 (3 H, s, ArOMe), 5.97 (1 H, s, ArCH), 6.85, 7.15 (2 H, d, J 9 Hz, aromatic H), and 6.89 (1 H, d, J 1.4 Hz, CH=CMe); δ_C 168.56 (C=O), 159.35 (arene COMe), 153.16 (COMe), 134.82 (CHCMe), 130.70 (CH=CMe), 130.16, 128.78, 113.78 (aromatic C), 108.77 (ArCH), 55.01 (ArOMe), 54.73 (COMe), 51.86 (CO$_2Me$), and 13.80 (Me).

Methyl 4-methoxy-5-(2-methoxyphenyl)-2-methylpenta-2,4-dienoate (**24**). Work-up and purification afforded an oil identified as a 3:2 mixture of the 2E,4E and 2E,4Z isomers (Found: C, 68.6; H, 6.9%; M^+, 262.1199. C$_{15}$H$_{18}$O$_4$ requires C, 68.67; H, 6.92%; M, 262.1200).

2E,4E Isomer; δ_H 2.13 (3 H, br s, CH=CMe), 3.73 (3 H, s, COMe), 3.80 (3 H, s, CO$_2$Me), 3.85 (3 H, s, ArOMe), 6.21 (1 H, br s, ArCH), 6.85–7.40 (5 H, m, aromatic H and CH=CMe); δ_C 167.89 (C=O), 156.17 (arene COMe), 153.44 (COMe), 134.18 (CH=CMe), 129.27 (CH=CMe), 128.08, 124.56, 119.56, 114.46, 109.54 (aromatic C), 103.84 (ArCH), 63.67 (COMe), 56.84 (ArOMe), 50.71 (CO$_2Me$), and 12.65 (Me).

2E,4Z Isomer; δ_H 2.24 (3 H, br s, CH=CMe), 3.60 (3 H, s, COMe), 3.81 (3 H, s, CO$_2$Me), 3.85 (3 H, s, ArOMe), 6.52 (1 H, br s, ArCH), 6.84–7.4 (4 H, m, aromatic H and CH=CMe), and 8.12 (1 H, dd, aromatic H); δ_C 167.99 (C=O), 156.19 (arene COMe), 153.24 (COMe), 134.20 (CH=CMe), 129.29 (CH=CMe), 126.84, 124.54, 119.36, 114.22, 109.52 (aromatic C), 104.14 (ArCH), 63.87 (COMe), 56.90 (ArOMe), 50.70 (CO$_2$Me), and 13.38 (Me).

Methyl 5-(2-allyloxyphenyl)-4-methoxy-2-methylpenta-2,4-di-enoate (**25**). 2E,4E Isomer, oil (Found: C, 70.6; H, 7.1%; M^+, 288.1316. C$_{17}$H$_{20}$O$_4$ requires C, 70.80; H, 6.99%; M, 288.1356); δ_H 2.16 (3 H, br s, CH=CMe), 3.66 (3 H, s, OMe), 3.68 (3 H, s,

CO_2Me), 4.53 (2 H, d, J 4 Hz, OCH_2), 5.22–5.56 (2 H, m, $CH=CH_2$), 5.95–6.22 (1 H, m, $CH=CH_2$), 6.30 (1 H, s, $ArCH$), 6.82 (1 H, s, $CH=CO_2Me$), and 6.96–7.37 (4 H, m, aromatic H); δ_C 168.66 (C=O), 156.03 (arene $COMe$), 154.15 ($COMe$), 135.20 ($CH=CCO_2Me$), 133.70 ($CH=CCO_2Me$), 131.12, 129.02, 128.71, 125.67, 120.94, 111.89 (aromatic C and $CH=CH_2$), 116.81 ($CH=CH_2$), 104.61 (ArCH), 68.97 (ArOCH_2), 58.80 (CO_2Me), 57.86 (OMe), and 23.50 ($CH=CMe$).

$2E,4Z$ Isomer, oil (Found: M^+, 288.1324. $C_{17}H_{20}O_4$ requires M, 288.1356); δ_H 2.20 (3 H, br s, $CH=CMe$), 3.58 (3 H, s, OMe), 3.68 (3 H, s, CO_2Me), 4.53 (2 H, d, J 4 Hz, OCH_2), 5.22–5.56 (2 H, m, $CH=CH_2$), 5.93–6.22 (1 H, m, $CH=CH_2$), 6.28 (1 H, s, ArCH), 6.60 (1 H, s, $CH=CCO_2Me$), and 6.96–7.37 (4 H, m, aromatic H); δ_C 168.35 (C=O), 155.91 (arene $COMe$), 153.78 ($COMe$), 135.20 ($CH=CCO_2Me$), 133.69 ($CH=CCO_2Me$), 130.41, 128.62, 127.98, 124.40, 120.57, 112.19 (aromatic C and $CH=CH_2$), 117.29 ($CH=CH_2$), 104.61 (ArCH), 69.21 (OCH_2), 58.80 (CO_2Me), 54.86 (OMe), and 25.86 ($CH=CMe$).

Methyl 5-cyclohexyl-4-methoxy-2-methylpenta-2,4-dienoate (**26**). Work-up and purification afforded an oil identified as a mixture (3:1) of $2E,4E$ and $2E,4Z$ isomers (Found: C, 70.6; H, 9.0%; M^+, 238.1570. $C_{14}H_{22}O_3$ requires C, 70.54; H, 9.31%; M, 238.1563).

$2E,4E$ Isomer; δ_H 1.1–1.7 (10 H, m, $[CH_2]_5$), 2.09 (3 H, s, Me), 2.13–2.34 (1 H, m, $CHCH=$), 3.58 (3 H, s, OMe), 3.80 (3 H, s, CO_2Me), 4.73 (1 H, d, J 9 Hz, $CHCH=$), and 7.36 (1 H, br s, $CH=CCO_2Me$); δ_C 168.25 (C=O), 150.71 ($COMe$), 129.30 ($CH=CMe$), 128.24 ($CH=CMe$), 113.55 ($CH=COMe$), 53.32 (CO_2Me), 50.89 (OMe), 35.59 ($CHCH=$), 33.86, 28.64, 25.30 $[CH_2]_5$, and 13.38 (Me).

$2E,4Z$ Isomer; δ_H 1.1–1.8 (10 H, m, $[CH_2]_5$), 2.07 (3 H, s, Me), 2.1–2.37 (1 H, m, $CHCH=$), 3.52 (3 H, s, OMe), 3.77 (3 H, s, CO_2Me), 5.13 (1 H, d, J 9 Hz, $CHCH=$), and 7.03 (1 H, br s, $CH=CCO_2Me$).

Methyl 4-methoxy-2,6-dimethylhepta-2,4-dienoate (**27**). $2E,4E$ Isomer, oil (Found: C, 66.8; H, 9.0; M^+, 198.1525. $C_{11}H_{18}O_3$ requires C, 66.62; H, 9.16%; M, 198.1251); δ_H 1.26 (6 H, d, J 4 Hz, $CHMe_2$), 2.11 (3 H, d, J 1.5 Hz, $CH=CMe$), 2.60 (1 H, m, $CHMe_2$), 3.57 (3 H, s, OMe), 3.78 (3 H, s, CO_2Me), 4.72 (1 H, d, J 9 Hz, $CH=COMe$), and 7.40 (1 H, d, J 9 Hz, $CH=CCO_2Me$); δ_C 167.57 (C=O), 151.46 ($COMe$), 129.54 ($CH=CMe$), 128.78 ($CH=CCO_2Me$), 114.98 ($CH=COMe$), 54.39 ($COMe$), 52.38 (CO_2Me), 27.63 ($CHMe_2$), 24.70 ($CHMe_2$), and 14.15 ($CH=CMe$).

$2E,4Z$ Isomer, oil (Found: M^+, 198.1300. $C_{11}H_{18}O_3$ requires M, 198.1251); δ_H 1.26 (6 H, d, J 4 Hz, $CHMe_2$), 2.11 (3 H, d, J 1.5 Hz, $CH=CMe$), 2.75 (1 H, m, $CHMe_2$), 3.54 (3 H, s, OMe), 3.78 (3 H, s, CO_2Me), 5.1 (1 H, d, J 9 Hz, $CH=COMe$), and 7.04 (1 H, d, J 9 Hz, $CH=CCO_2Me$); δ_C 168.05 (C=O), 149.82 ($COMe$), 129.73 ($CH=CMe$), 128.78 ($CH=CCO_2Me$), 114.98 ($CH=COMe$), 54.39 ($COMe$), 51.74 (CO_2Me), 27.63 ($CHMe_2$), 24.70 ($CHMe_2$), and 14.15 ($CH=CMe$).

Methyl 4-methoxy-2-methylnona-2,4-dienoate (**28**). $2E,4E$ Isomer, oil (Found: C, 67.7; H, 9.6. $C_{12}H_{20}O_3$ requires C, 67.88; H, 9.50%); δ_H 0.91 (3 H, m, CH_2Me), 1.4–1.6 (4 H, m, $[CH_2]_2Me$), 2.11 (3 H, d, J 1.4 Hz, $CH=CMe$), 2.24 (2 H, m, $C=CHCH_2$), 3.6 (3 H, s, COMe), 3.81 (3 H, s, CO_2Me), 4.89 (1 H, t, J 7.5 Hz, $C=CHCH_2$), and 7.36 (1 H, br s, $CH=CCO_2Me$).

$2E,4Z$ Isomer, oil (Found: C, 67.8; H, 9.7. $C_{12}H_{20}O_3$ requires C, 67.88; H, 9.50%); δ_H 0.92 (3 H, m, CH_2Me), 1.2–1.65 (4 H, m, $[CH_2]_2Me$), 2.11 (3 H, s, $CH=CMe$), 2.3 (2 H, m, $C=CHCH_2$), 3.54 (3 H, s, COMe), 3.81 (3 H, s, CO_2Me), 5.29 (1 H, t, J 7.5 Hz, $C=CHCH_2$), and 7.08 (1 H, br s, $CH=CCO_2Me$).

Methyl 4-methoxy-2-methyltetradeca-2,4-dienoate (**29**). $2E,4E$ Isomer, oil (Found: C, 72.4; H, 10.7. $C_{17}H_{30}O_3$ requires C, 72.28; H, 10.71%); δ_H 0.89 (3 H, t, J 5.5 Hz, CH_2Me), 1.0–1.85 (14 H, m, $[CH_2]_7$), 2.0 (3 H, d, J 1 Hz, $CH=CMe$), 2.18 (2 H, m, $C=CHCH_2$), 3.54 (3 H, s, COMe), 3.69 (3 H, s, CO_2Me), 4.7 (1

H, t, J 7.5 Hz, $C=CHCH_2$), and 7.11 (1 H, d, J 1 Hz, $CH=CCO_2Me$).

$2E,4Z$ Isomer, oil (Found: C, 72.5; H, 10.9. $C_{17}H_{30}O_3$ requires C, 72.28; H, 10.71%); δ_H 0.86 (3 H, t, J 5.5 Hz, CH_2Me), 1.0–1.80 (14 H, m, $[CH_2]_7$), 2.02 (3 H, d, J 1 Hz, $CH=CMe$), 2.15 (2 H, m, $C=CHCH_2$), 3.47 (3 H, s, COMe), 3.69 (3 H, s, CO_2Me), 5.11 (1 H, t, J 7.5 Hz, $C=CHCH_2$), and 6.87 (1 H, d, J 1 Hz, $CH=CCO_2Me$).

Ethyl 4-methoxy-5-(4-methoxyphenyl)-2-methylpenta-2,4-dienoate (**30**). $2E,4E$ Isomer, pale yellow oil (Found: C, 69.5; H, 7.2%; M^+, 276.1358. $C_{16}H_{20}O_4$ requires C, 69.53; H, 7.30%; M, 276.1356); δ_H 1.29 (3 H, t, J 7.6 Hz, OCH_2Me), 2.20 (3 H, br s, $CH=CMe$), 3.69 (3 H, s, OMe), 3.76 (3 H, s, ArOMe), 4.21 (2 H, q, J 7.6 Hz, OCH_2Me), 5.99 (1 H, s, ArCH), 6.87, 7.18 (2 × 2 H, d, J 9 Hz, aromatic H), and 7.40 (1 H, s, $CH=CCO_2Et$): δ_C 168.49 (C=O), 159.02 (arene $COMe$), 152.77 ($COMe$), 134.44 ($CH=CCO_2Et$), 130.91 ($CH=CCO_2Et$), 130.06, 127.58, 113.43 (aromatic C), 108.34 (ArCH), 60.25 (OCH_2Me), 57.27 (ArOMe), 54.54 (OMe), 13.98 ($CH=CMe$), and 13.32 (OCH_2Me).

$2E,4Z$ Isomer, pale yellow oil (Found: M^+, 276.1357. $C_{16}H_{20}O_4$ requires M, 276.1356); δ_H 1.23 (3 H, t, J 7.6 Hz, OCH_2Me), 2.12 (3 H, br s, $CH=CMe$), 3.58 (3 H, s, OMe), 3.76 (3 H, s, ArOMe), 4.17 (2 H, q, J 7.6 Hz, OCH_2Me), 5.97 (1 H, s, ArCH), 6.87, 7.18 (2 × 2 H, d, J 9 Hz, aromatic H), and 6.93 (1 H, s, $CH=CCO_2Et$); δ_C 167.83 (C=O), 159.02 (arene $COMe$), 152.77 ($COMe$), 134.45 ($CH=CCO_2Et$), 130.06, 127.21, 113.61 (aromatic C), 128.43 ($CH=CCO_2Et$), 108.34 (ArCH), 64.13 (OCH_2Me), 57.27 (ArOMe), 54.30 (OMe), 13.98 ($CH=CMe$), and 13.32 (OCH_2Me).

Ethyl 4-methoxy-5-(p-tolyl)-2-methylpenta-2,4-dienoate (**31**). Obtained as an oil which was a 4:1 mixture of the $2E,4E$ and $2E,4Z$ isomers (Found: C, 74.1; H, 7.5%; M^+, 260.1477. $C_{16}H_{20}O_3$ requires C, 73.81; H, 7.75%; M, 260.1407).

$2E,4E$ Isomer; δ_H 1.28 (3 H, t, J 6.9 Hz, OCH_2Me), 2.17 (3 H, d, J 1.1 Hz, $CH=CMe$), 2.36 (3 H, s, ArMe), 3.71 (3 H, s, OMe), 4.23 (2 H, q, J 6.9 Hz, OCH_2Me), 6.06 (1 H, s, ArCH), 7.14 (4 H, br s, aromatic H), and 7.18 (1 H, br s, $CH=CCO_2Et$); δ_C 167.84 (C=O), 152.93 ($COMe$), 135.28 ($CH=CCO_2Et$), 132.78 ($CH=CCO_2Et$), 130.67, 128.52, 125.63, 120.24 (aromatic C), 108.07 (ArCH), 60.04 (OCH_2Me), 54.09 (OMe), 20.41 (ArMe), 13.85 ($CH=CMe$), and 13.61 (OCH_2Me).

$2E,4Z$ Isomer; δ_H 1.32 (3 H, t, J 6.8 Hz, OCH_2Me), 2.23 (3 H, d, J 1.1 Hz, $CH=CMe$), 2.36 (3 H, s, ArMe), 3.62 (3 H, s, OMe), 4.30 (2 H, q, J 6.8 Hz, OCH_2Me), 6.01 (1 H, s, ArCH), and 7.15 (5 H, m, aromatic H and $CH=CCO_2Et$); δ_C 167.84 (C=O), 153.09 ($COMe$), 136.78 ($CH=CCO_2Et$), 131.75 ($CH=CCO_2Et$), 130.13, 128.36, 125.02, 120.00 (aromatic C), 108.22 (ArCH), 60.15 (OCH_2Me), 54.08 (OMe), 20.61 (ArMe), 13.70 ($CH=CMe$), and 12.96 (OCH_2Me).

Ethyl 4-methoxy-2-methyl-5-(2-prop-2-ynyloxyphenyl)penta-2,4-dienoate (**32**). Work-up and purification afforded a syrup which was identified as a 5:1 mixture of $2E,4E$ and $2E,4Z$ isomers) Found: C, 72.1; H, 6.5%; M^+, 300.1316. $C_{18}H_{20}O_4$ requires C, 71.97; H, 6.72%; M, 300.1356).

$2E,4E$ Isomer; δ_H 1.31 (3 H, t, J 7.5 Hz, OCH_2Me), 2.20 (3 H, d, J 1.2 Hz, $CH=CMe$), 2.48 (1 H, br s, $C\equiv CH$), 3.59 (3 H, s, OMe), 4.21 (2 H, q, J 7.5 Hz, OCH_2Me), 4.66 (2 H, d, J 2.9 Hz, ArOCH_2), 6.39 (1 H, s, ArCH), and 6.90–7.22 (5 H, m, aromatic H and $CH=CCO_2Et$); δ_C 168.63 (C=O), 154.87 (arene $COCH_2$), 154.17 ($COMe$), 134.87 ($CH=CCO_2Et$), 131.39–112.28 (aromatic C and $CH=CCO_2Et$), 103.99 (ArCH), 78.79, 78.63 ($C\equiv CH$), 60.84 (OCH_2Me), 56.38 (ArOCH_2), 54.93 (OMe), 14.41 ($CH=CMe$), and 14.22 (OCH_2Me).

$2E,4Z$ Isomer; δ_H 1.25 (3 H, t, J 7.5 Hz, OCH_2Me), 2.09 (3 H, d, J 1.2 Hz, $CH=CMe$), 2.4 (1 H, br s, $C\equiv CH$), 3.73 (3 H, s, OMe), 4.18 (2 H, q, J 7.5 Hz, OCH_2Me), 4.65 (2 H, d, J 2.9 Hz, ArOCH_2), 6.15 (1 H, s, ArCH), and 6.95–7.24 (5 H, m, aromatic H and $CH=CCO_2Et$); δ_C 168.40 (C=O), 154.76 (arene $COCH_2$),

153.85 (COMe), 134.52 (CH=CCO$_2$Et), 131.40–112.30 (aromatic C and CH=CCO$_2$Et), 104.00 (ArCH), 75.80, 75.60 (C≡CH), 60.68 (OCH$_2$Me), 56.06 (ArOCH$_2$), 57.90 (OMe), 14.38 (CH=CMe), and 13.71 (OCH$_2$Me).

Ethyl (2E)-4-methoxy-2-methylpenta-2,4-dienoate (**33**). Obtained as an oil (Found: C, 63.6; H, 8.1%; M^+, 170.0984. C$_9$H$_{14}$O$_3$ requires C, 63.49; H, 8.29%; M, 170.0939); δ_H 1.24 (3 H, q, J 8.2 Hz, OCH$_2$Me), 2.08 (3 H, br s, CH=CMe), 3.51 (3 H, s, OMe), 4.10 (2 H, q, J 8.2 Hz, OCH$_2$Me), 4.25 (2 H, br s, C=CH$_2$), and 6.80 (1 H, br s, CH=CCO$_2$Et); δ_C 168.54 (C=O), 159.39 (COMe), 133.49 (CH=CCO$_2$Et), 129.02 (CH=CCO$_2$Et), 91.76 (C=CH$_2$), 60.64 (OCH$_2$Me), 54.62 (OMe), 14.09 (CH=CMe), and 13.75 (OCH$_2$Me).

Ethyl 4-methoxy-2-methylhexa-2,4-dienoate (**34**). Work-up and purification afforded an oil which was identified as a 5:3 mixture of 2E,4E and 2E,4Z isomers (Found: C, 65.2; H, 8.9%; M^+, 184.1102. C$_{10}$H$_{16}$O$_3$ requires C, 65.18; H, 8.76%; M, 184.1095).

2E,4E Isomer; δ_H 1.27 (3 H, t, J 7.4 Hz, OCH$_2$Me), 1.67 (3 H, d, J 8.4 Hz, C=CHMe), 2.03 (3 H, br s, CH=CMe), 3.46 (3 H, s, OMe), 4.11 (2 H, q, J 7.4 Hz, OCH$_2$Me), 4.77 (1 H, q, J 8.4 Hz C=CHMe), and 7.09 (1 H, br s, CH=CCO$_2$Et); δ_C 168.62 (C=O), 152.60 (COMe), 129.61 (CH=CCO$_2$Et), 129.49 (CH=CCO$_2$Et), 101.38 (C=CHMe), 60.60 (OCH$_2$Me), 54.32 (OMe), 14.12, 14.08 (2 × C=CMe), and 12.05 (OCH$_2$Me).

2E,4Z Isomer; δ_H 1.25 (3 H, t, J 7.4 Hz, OCH$_2$Me), 1.69 (3 H, d, J 8.4 Hz C=CHMe), 2.02 (3 H, br s, CH=CMe), 3.45 (3 H, s, OMe), 4.14 (2 H, q, J 7.4 Hz, OCH$_2$Me), 5.12 (1 H, q, J 8.4 Hz, C=CHMe), and 6.78 (1 H, br s, CH=CCO$_2$Et).

Ethyl 4-methoxy-2-methylhepta-2,4-dienoate (**35**). 2E,4E Isomer, oil (Found: C, 66.4; H, 9.0%; M^+, 198.1344. C$_{11}$H$_{18}$O$_3$ requires C, 66.62; H, 9.16%; M, 198.1251); δ_H 0.96 (3 H, t, J 7.5 Hz, MeCH$_2$CH=), 1.20 (3 H, t, J 7.6 Hz, OCH$_2$Me), 1.41–1.60 (2 H, m, MeCH$_2$CH=), 1.99 (3 H, br s, CH=CMe), 3.35 (3 H, s, OMe), 4.00 (2 H, q, J 7.6 Hz, OCH$_2$Me), 4.60 (1 H, t, J 7 Hz, MeCH$_2$CH=), and 7.00 (1 H, br s, CH=CCO$_2$Et); δ_C 168.02 (C=O), 151.44 (COMe), 129.19 (CH=CCO$_2$Et), 128.96 (CH=CCO$_2$Et), 108.68 (MeCH$_2$CH=), 60.07 (OCH$_2$Me), 53.65 (OMe), 19.82 (MeCH$_2$CH=), 14.65 (C=CMe), 13.69 (OCH$_2$-Me), and 13.60 (MeCH$_2$CH=).

2E,4Z Isomer, oil (Found: M^+, 198.1306. C$_{11}$H$_{18}$O$_3$ requires M, 198.1251); δ_H 0.94 (3 H, t, J 7.5 Hz, MeCH$_2$CH=), 1.20 (3 H, t, J 7.6 Hz, OCH$_2$Me), 1.43–1.59 (2 H, m, MeCH$_2$CH=), 2.00 (3 H, br s, CH=CMe), 3.33 (3 H, s, OMe), 4.02 (2 H, q, J 7.6 Hz, OCH$_2$Me), 4.82 (1 H, t, J 7 Hz, MeCH$_2$CH=), and 6.68 (1 H, br s, CH=CCO$_2$Et); δ_C 168.02 (C=O), 152.52 (COMe), 133.47 (CH=CCO$_2$Et), 128.96 (CH=CCO$_2$Et), 108.92 (MeCH$_2$CH=), 60.07 (OCH$_2$Me), 58.20 (OMe), 18.42 (MeCH$_2$CH=), 14.65 (C=CMe), 13.69 (OCH$_2$Me), and 13.44 (MeCH$_2$CH=).

Ethyl 4-methoxy-2,6-dimethylhepta-2,4-dienoate (**36**). 2E,4E Isomer, oil (Found: C, 68.1; H, 9.3%; M^+, 212.1586. C$_{12}$H$_{20}$O$_3$ requires C, 67.88; H, 9.50%; M, 212.1407); δ_H 1.06 (6 H, d, J 7 Hz, CHMe$_2$), 1.24 (3 H, t, J 7.2 Hz, OCH$_2$Me), 2.08 (3 H, br s, CH=CMe), 2.60 (1 H, m, CHMe$_2$), 3.50 (3 H, s, OMe), 4.10 (2 H, q, J 7.2 Hz, OCH$_2$Me), 4.58 (1 H, d, J 9.5 Hz, CH=COMe), and 7.17 (1 H, br s, CH=CCO$_2$Et); δ_C 168.03 (C=O), 151.03 (COMe), 129.24 (CH=CCO$_2$Et), 128.90 (CH=CCO$_2$Et), 114.88 (CH=COMe), 60.06 (OCH$_2$Me), 53.59 (OMe), 26.25 (CHMe$_2$), 23.58 (CHMe$_2$), 13.71 (CH=CMe), and 13.60 (OCH$_2$Me).

2E,4Z Isomer, oil (Found: M^+, 212.1560. C$_{12}$H$_{20}$O$_3$ requires M, 212.1407); δ_H 1.05 (6 H, d, J 7 Hz, CMe$_2$), 1.24 (3 H, t, J 7.2 Hz, OCH$_2$Me), 2.06 (3 H, br s, CH=CMe), 2.78 (1 H, m, CHMe$_2$), 3.48 (3 H, s, OMe), 4.12 (2 H, q, J 7.2 Hz, OCH$_2$Me), 4.90 (1 H, d, J 9.5 Hz, CH=COMe), and 6.78 (1 H, br s, CH=CCO$_2$Et); δ_C 167.68 (C=O), 150.36 (COMe), 129.41 (CH=CCO$_2$Et), 128.90 (CH=CCO$_2$Et), 115.12 (CH=COMe), 60.06 (OCH$_2$Me), 53.59 (OMe), 26.25 (CHMe$_2$), 23.58 (CHMe$_2$), 13.71 (CH=CMe), and 13.60 (OCH$_2$Me).

Allyl 4-methoxy-5-(4-methoxyphenyl)-2-methylpenta-2,4-dienoate (**37**). Work-up and purification afforded an oil which was identified as a 2:1 mixture of 2E,4E and 2E,4Z isomers (Found: C, 71.0; H, 6.7%; M^+, 288.1370. C$_{17}$H$_{20}$O$_4$ requires C, 70.80; H, 6.99%; M, 288.1356).

2E,4E Isomer; δ_H 2.12 (3 H, d, J 1.4 Hz, CH=CMe), 3.70 (3 H, s, OMe), 3.79 (3 H, s, ArOMe), 4.64 (2 H, d, J 6 Hz, OCH$_2$), 5.24 (2 H, m, CH=CH$_2$), 5.95 (1 H, m, CH=CH$_2$), 5.97 (1 H, s, ArCH), 6.87, 7.14 (2 × 2 H, d, J 9 Hz, aromatic H), and 7.36 (1 H, br s, CH=CMe); δ_C 168.18 (C=O), 158.34 (arene COMe), 152.92 (COMe), 135.21 (CH=CMe), 132.57 (CH=CMe), 131.62 (CH=CH$_2$), 130.34, 128.63, 113.94 (aromatic C), 117.30 (CH=CH$_2$), 108.79 (ArCH), 65.19 (OCH$_2$), 57.82 (ArOMe), 55.07 (OMe), and 14.47 (CH=CMe).

2E,4Z Isomer; δ_H 2.02 (3 H, d, J 1.4 Hz, CH=CMe), 3.58 (3 H, s, OMe), 3.79 (3 H, s, ArOMe), 4.67 (2 H, d, J 7 Hz, OCH$_2$), 5.26 (2 H, m, CH=CH$_2$), 5.95 (1 H, m, CH=CH$_2$), 5.96 (1 H, s, ArCH), 6.89, 7.16 (2 × 2 H, d, J 9 Hz, aromatic C), and 7.63 (1 H, d, J 1.4 Hz, CH=CMe); δ_C 167.94 (C=O), 159.21 (arene COMe), 152.78 (COMe), 135.19 (CH=CMe), 132.43 (CH=CMe), 131.62 (CH=CH$_2$), 130.59, 128.63, 113.75 (aromatic C), 117.5 (CH=CH$_2$), 108.80 (ArCH), 65.44 (OCH$_2$), 57.81 (ArOMe), 54.78 (OMe), and 13.47 (CH=CMe).

Ethyl 5-(2-allyloxyphenyl)-4-methoxy-3-methylpenta-2,4-dienoate (**38**). Work-up and purification furnished an oil which was identified as a 10:1 mixture of 2E,4E and 2E,4Z isomers (Found: C, 71.2; H, 7.5%; M^+, 302.1640. C$_{18}$H$_{22}$O$_4$ requires C, 71.49; H, 7.34%; M, 302.1512).

2E,4E Isomer; δ_H 1.30 (3 H, t, J 7.1 Hz, OCH$_2$Me), 2.44 (3 H, d, J 1.2 Hz, CH=CMe), 3.59 (3 H, s, OMe), 4.18 (2 H, q, J 7.1 Hz, OCH$_2$Me), 4.52 (2 H, d, J 4.9 Hz, ArOCH$_2$), 5.40 (2 H, m, CH=CH$_2$), 6.02 (1 H, m, CH=CH$_2$), 6.34 (1 H, s, C=CHCO$_2$Et), 6.80–7.20 (4 H, m, aromatic H), and 6.84 (1 H, s, ArCH); δ_C 166.89 (C=O), 156.03 (arene COMe), 154.79 (COMe), 148.93 (C=CHCO$_2$Et), 132.68, 129.24, 128.39, 126.02, 116.58, 115.35 (aromatic C and CH=CH$_2$), 123.67 (C=CHCO$_2$Et), 116.71 (CH=CH$_2$), 111.28 (ArCH), 68.37 (ArOCH$_2$), 64.47 (OCH$_2$Me), 58.25 (OMe), and 14.25, 13.81 (2 × Me).

2E,4Z Isomer; δ_H 1.33 (3 H, t, J 7.1 Hz, OCH$_2$Me), 2.24 (3 H, d, J 1.2 Hz, CH=CMe), 3.43 (3 H, s, OMe), 4.09 (2 H, q, J 7.1 Hz, OCH$_2$Me), 4.54 (2 H, d, J 5 Hz, ArOCH$_2$), 5.65 (2 H, m, CH=CH$_2$), 5.88 (1 H, s, C=CHCO$_2$Et), 6.00 (1 H, m, CH=CH$_2$), 6.88–7.35 (5 H, m, aromatic H and ArCH).

General Procedure for the Hydrolysis of the Methoxy Diene Esters to β,γ-Unsaturated Ketoesters.—The appropriate methoxy diene ester (10 mmol), dissolved in a 1:1 mixture of methanol and THF (50 ml), was treated with 2M aqueous HCl (15 ml). The solution was stirred at room temperature for 4 d after which time the organic solvent was evaporated and the remaining mixture extracted with ether (3 × 30 ml). The combined organic extracts were washed successively with saturated aqueous NaHCO$_3$ and brine prior to drying over Na$_2$SO$_4$. Filtration and removal of solvent gave the crude product which was purified by dry column chromatography [light petroleum (b.p. 40–60 °C)–Et$_2$O (2:1); silica].

Methyl 5-(4-methoxyphenyl)-2-methyl-4-oxopent-2-enoate (**41**). Obtained as an oil (Found: C, 67.9; H, 6.4%; M^+, 248.1058. C$_{14}$H$_{16}$O$_4$ requires C, 67.71; H, 6.50%; M, 248.1044); δ_H 2.18 (3 H, d, J 2 Hz, Me), 3.67 (2 H, s, CH$_2$), 3.78 (6 H, s, OMe), and 6.65–7.8 (5 H, aromatic H and CH=CCO$_2$Me); δ_C 202.19 (C=O), 168.32 (CO$_2$Me), 158.72 (arene COMe), 141.36, 131.70, 130.36, 125.27, 114.16 (aromatic C and CH=CCO$_2$Me), 55.27 (ArOMe), 52.53, 50.53 (CO$_2$Me, CH$_2$), and 14.17 (Me).

Methyl 5-(2-methoxyphenyl)-2-methyl-4-oxopent-2-enoate (**42**). Obtained as an oil (Found: C, 67.8; H, 6.3%; M^+, 248.1048. C$_{14}$H$_{16}$O$_4$ requires C, 67.71; H, 6.50%; M, 248.1044); δ_H 2.20 (3 H, d, J 2 Hz, Me), 3.67 (2 H, s, CH$_2$), 3.74, 3.77 (2 × 3 H,

C*H*=CCO₂Me); δ_C 202.40 (*C*=O), 168.32 (*C*O₂Me), 157.08 (arene *C*OMe), 139.78, 131.85, 128.30, 127.15, 122.23, 120.29, 110.21 (aromatic and *C*H=CHCO₂Me), 54.84 (ArO*Me*), 51.50 (CO₂*Me*), 44.34 (CH₂), and 13.74 (Me).

Methyl 2,6-dimethyl-4-oxohept-2-enoate (**43**). Obtained as an oil (Found: C, 65.4; H, 8.4. C₁₀H₁₆O₃ requires C, 65.18; H, 8.76%); δ_H 1.09 (6 H, d, *J* 7 Hz, CH*Me₂*), 2.15 (3 H, d, *J* 1.4 Hz, CH=C*Me*), 2.55 (2 H, d, *J* 7 Hz, CH₂), 2.63 (1 H, m, C*H*Me₂), 3.76 (3 H, s, CO₂Me), and 7.1 (1 H, br s, C*H*=CCO₂Me).

Methyl 2-methyl-4-oxonon-2-enoate (**44**). Obtained as an oil (Found: C, 66.8; H, 8.9. C₁₁H₁₈O₃ requires C, 66.62; H, 9.16%); δ_H 0.9 (3 H, t, *J* 6 Hz, CH₂*Me*), 0.95–1.8 (6 H, m, [C*H₂*]₃Me), 2.2 (3 H, br s, CH=C*Me*), 2.52 (2 H, t, *J* 7.5 Hz, CH₂CO), 3.73 (3 H, s, CO₂Me), and 7.11 (1 H, br s, C*H*=CCO₂Me).

Methyl 2-methyl-4-oxotetradec-2-enoate (**45**). Obtained as an oil (Found: C, 71.8; H, 10.3. C₁₆H₂₈O₃ requires C, 71.59; H, 10.52%); δ_H 0.90 (3 H, t, *J* 5.5 Hz, CH₂*Me*), 1.0–1.88 (16 H, m, [C*H₂*]₈Me), 2.0 (3 H, d, *J* 1 Hz, CH=C*Me*), 2.54 (2 H, t, *J* 7 Hz, CH₂CO), 3.69 (3 H, s, CO₂Me), and 7.11 (1 H, d, *J* 1 Hz, C*H*=CCO₂Me).

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