Silyl enol ethers as new protecting groups for alkyl 4-halo-3-oxobutanoates; the preparation of pure (3-alkoxycarbonyl-2-oxopropyl)triphenylphosphonium salts

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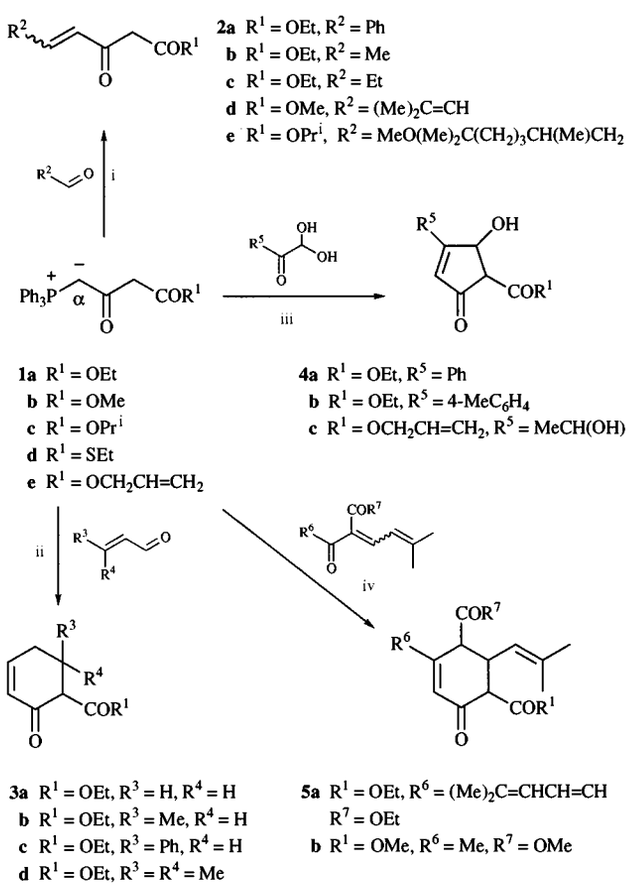
A new method has been developed for the preparation of pure (3-alkoxycarbonyl-2-oxopropyl)triphenylphosphonium salts 8. Alkyl 4-bromo-3-oxobutanoates and alkyl 4-chloro-3-oxobutanoates 7 are protected as the trimethylsilyl enol ethers prior to treatment of the resulting bromo(trimethylsilyl enol ether) esters 20c and 21c with triphenylphosphine in toluene and then addition of a little water to give pure (3-isopropoxycarbonyl-2-oxopropyl)triphenylphosphonium bromide 8c. Bromo(silyl enol ether) esters react more efficiently with triphenylphosphine than the chloro(silyl enol ether) esters. *tert*-Butyldimethylsilyl enol ethers of alkyl 4-bromo-3-oxobutanoates and alkyl 4-chloro-3-oxobutanoates 7 also react with triphenylphosphine. Protection of isopropyl 4-bromo-3-oxobutanoate 7c as the enol acetate followed by subsequent reaction with triphenylphosphine gives (*Z*)-(2-acetoxy-3-isopropoxycarbonylbut-2-enyl)triphenylphosphonium bromide 17.

Introduction

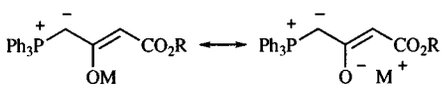
More than three decades ago, ethyl 3-oxo-4-(triphenylphosphoranylidene)butanoate **1a** was introduced[1] as a potentially useful phosphonium ylide.[2] However, it soon became clear that this phosphonium ylide **1** is one of the more difficult ylides to use.[3] For example, condensation of the phosphonium ylide **1a** and benzaldehyde gave a 47%[1] (62%)[3a] yield of the expected *E*-Wittig product, the *E*-γ,δ-unsaturated-β-keto ester **2a** which is strongly enolisable (Scheme 1).[1] On the other hand, condensation of the phosphonium ylide **1a** with acetaldehyde did not give the expected γ,δ-unsaturated-β-keto ester **2b** but a low yield of the aldol product of acetaldehyde and the γ,δ-unsaturated-β-keto ester **2b**.[3a] Sporadic applications of the phosphonium ylides **1a**[4a,4c,4f] and **1b**[4d,4e] in syntheses followed for about 20 years. A sudden interest in phosphonium ylide **1** occurred when Bodalski *et al.* announced a very useful annulation technique.[5] Ethyl 3-oxo-4-(triphenylphosphoranylidene)-butanoate **1a** in the presence of 'wet' sodium hydride condensed with a number of α,β-unsaturated carbonyl compounds to give 6-substituted 2-oxocyclohex-3-enecarboxylates **3** (for example **3a**–**3c**).[5] This result can be described in terms of an initial Michael-attack of the γ-ylide of **1a** on the β-carbon of the α,β-unsaturated carbonyl compound followed by an intramolecular Wittig condensation.[6] This annulation technique was used by others in successful syntheses.[7–9] Recently, five-membered ring annulation techniques using **1a**[10a] and **1e**[10c,10d] have been developed for the preparation of 4-substituted 2-oxocyclopent-3-enecarboxylates **4** (for example **4a**–**4c**),[10] thereby securing a meaningful role for phosphonium ylide **1** in organic synthesis. The phosphonium ylide **1a** has recently attracted attention because it can be activated by 'wet' NaH. It can thereby be manipulated into reacting with aliphatic carbonyl compounds to give γ,δ-unsaturated-β-keto esters **2** with high *Z*-selectivity, for example **2b**–**2c**.[11]

For some time now, we have been interested in novel reactions of the phosphonium ylide **1**. As a further extension of the work of Pietrusiewicz *et al.*,[5] we have found that without activation (*i.e.* not using 'wet' sodium hydride), the phosphonium ylide **1a** reacts with sterically hindered α,β-unsaturated-α-alkoxycarbonyl ketones to give, *via* a Michael–Wittig condensation, 6-oxo-2-vinylcyclohex-4-ene-1,3-dicarboxylates **5**.[8,9] We also succeeded in dramatically increasing the yield of γ,δ-unsaturated-β-keto esters **2** obtained from the condensation of the lithium enolate of the phosphonium ylide **1**. This was generated by treatment of the phosphonium ylide **1** with LDA (the



Scheme 1 *Reagents and conditions:* i, C_6H_6, reflux, *E*-isomers **2a**[1,3a] or 'wet' NaH, *Z*-isomers **2b**–**2c**[11] or LDA, mixture of *E*- and *Z*-isomers **2d**[8,9] in THF at room temp.; ii, 'wet' NaH[5] **3a**–**3c** or NaOH, **3d**[8] in THF; iii, EtOH or MeOH, room temp.;[10] iv, C_6H_6, reflux[8,9] and see ref. 7(*d*), reflux, THF

γ-methylene group of the phosphonium ylide **1** was blocked for other and further carbonyl condensations), and either saturated- or β-hindered-α,β-unsaturated aldehydes.[8,9] We have thereby made two distinct pathways for Wittig condensations of α,β-unsaturated carbonyl compounds. When initiated by the more ionic sodium enolate of the phosphonium ylide **1** (Scheme 2),



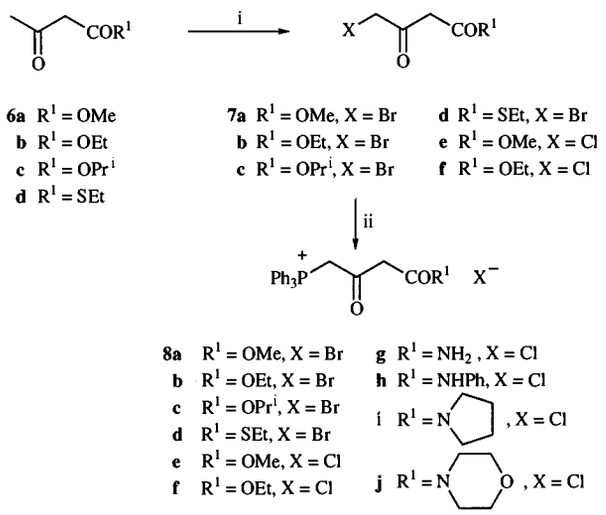
Scheme 2 M = Li, Na, K

the formation of substituted 2-oxocyclohex-3-enecarboxylates *e.g.* **3b** and **3d** results. However, the more covalent lithium enolate of the phosphonium ylide **1** predominantly produces a mixture of *E*- and *Z*-γ,δ-unsaturated-β-keto esters *e.g.* **2d** (Scheme 1).[8,9]

Despite the tremendous potential of the phosphonium ylide **1**, very little is known about the precursor (3-alkoxycarbonyl-2-oxopropyl)triphenylphosphonium salt **8**.[1,3a] In this paper we describe the preparation of pure phosphonium salt **8** and some of the characteristics of lithium and other metal enolates of the phosphonium salt **8**.

Results and discussion

As part of a programme aimed at developing synthetic routes for the preparation of new insect growth regulators from **2e** (Scheme 1), we had a need for pure (3-isopropoxycarbonyl-2-oxopropyl)triphenylphosphonium bromide **8c** (Scheme 3).



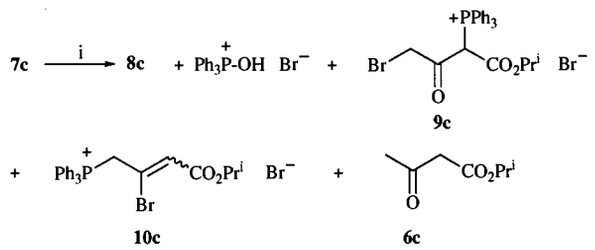
Scheme 3 *Reagents and conditions:* i, Br_2 in CH_2Cl_2 (for **7a**–**7d**); ii, Ph_3P in solvent 24 h (for **8a**–**8f**) or Ph_3P, heat without solvent (for **8e**, **8f**)

In general, (3-alkoxycarbonyl-2-oxopropyl)triphenylphosphonium salts **8a**–**8f** are prepared by adding alkyl 4-halo-3-oxobutanoates **7a**–**7f** to triphenylphosphine in a solvent, usually benzene.[1,3a,9] In an attempt to substitute a different solvent for benzene, pure isopropyl 4-bromo-3-oxobutanoate **7c**[12] was added to triphenylphosphine (Ph_3P) in anhydrous diethyl ether. To our dismay a mixture of (3-isopropoxycarbonyl-2-oxopropyl)triphenylphosphonium bromide **8c** and hydroxytriphenylphosphonium bromide,[13b,13i] in a ratio of 4:1, precipitated. Isopropyl 4-bromo-3-oxobutanoate **7c** and isopropyl-3-oxobutanoate **6c** were also isolated from the ether solution (Scheme 4). This result was not entirely unexpected. Previous preparation of the phosphonium bromide **8b** from ethyl 4-bromo-3-oxobutanoate **7b** and Ph_3P in methanol gave ethyl 3-oxobutanoate **6b** (78%), Ph_3P=O (89%) and a little of the phosphonium bromide **8b** (<4%).[3a] It was postulated that the formation of **6b** and Ph_3P=O was due to the solvolysis of an

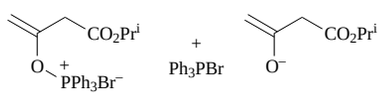
Table 1

Solvent	Yield of products (%) **8c**	**7c**	**6c**	Salts[a]
Cyclohexane	63	9	18	10
Dichloromethane	69	10	10	11
Acetone	76	9	9	6
Diethyl ether	80	10	2	8
Toluene	84	3	5	8
Tetrahydrofuran	85	2	8	5
Tetrachloromethane	86	3	4	7
Acetonitrile	86	4	5	5
Benzene	86	4	5	5

[a] Including **9c**, **10c** but not $Ph_3P^+OHBr^-$.



Scheme 4 *Reagents and conditions:* i, Ph_3P in an appropriate solvent (see Table 1)



11c **12c**

intermediate enol phosphonium salt.[3a,13] Enol phosphonium bromides prepared from α-bromo ketones are very sensitive towards moisture and will quickly hydrolyse to form debrominated ketones, Ph_3P=O and hydrobromic acid.[13,14] Chloroform and benzene gave much higher yields of **8b**.

The quaternisation of pure isopropyl 4-bromo-3-oxobutanoate **7c** and Ph_3P was repeated in anhydrous $CDCl_3$ and studied by ^1H NMR spectroscopy at room temperature. An exothermic reaction resulted, and within 15 min the solution became pale yellow. The reaction had finished after 30 min. Analysis of the ^1H NMR spectrum showed a mixture of the expected phosphonium salt **8c**, isopropyl 3-oxobutanoate **6c**, and apparently, unreacted isopropyl 4-bromo-3-oxobutanoate **7c**. Liquid secondary ion mass spectrometry (LSIMS) revealed two molecular ions attributed to the bromoketophosphonium bromide **9c** and the bromovinylphosphonium bromide **10c** in a combined yield of about 5%.[15] However, at no stage could a trace of the enol phosphonium bromide **11c** be found. This implies that strong enolization of the bromo ester (~22% in $CDCl_3$ at room temperature) results in protonation of the enolate bromophosphonium ion pair **12c**, leading to the formation of isopropyl 3-oxobutanoate **6c** (Scheme 4).[13e] The reaction of pure (>99%) 1-methylethyl 4-bromo-3-oxobutanoate **7c**[12] and triphenylphosphine in different solvents and under various conditions is summarised in Table 1.

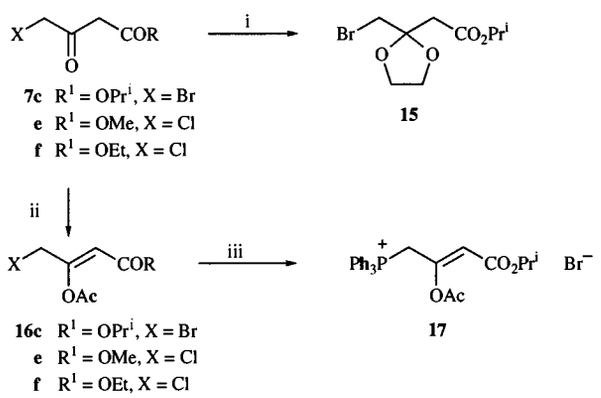
The addition of alkyl 4-bromo-3-oxobutanoates **7a**–**7d**[15] to triphenylphosphine gave at the most an 86 ± 2% yield of (3-alkoxycarbonyl-2-oxopropyl)triphenylphosphonium bromides **8a**–**8d**. Changing the reaction temperature to −10 °C and 55 °C in $CDCl_3$, or changing the addition procedure by adding triphenylphosphine to the bromo ester **7**, had only a slight effect on the yield of the phosphonium salts **8**. Using 2 mol equiv. of Ph_3P to bromo ester **7c** actually increased the formation of $Ph_3P^+OH\ Br^-$. Using DMSO as a solvent had a disastrous effect on the formation of **8c**, presumably because reactive intermediates attacked the solvent too. Initially, performing the

same reaction in wet $CDCl_3$ showed little difference in the ratio of products formed, but after 24 h, the acidic solution decarboxylated some of the phosphonium salt **8c** and led to the formation of (2-oxopropyl)triphenylphosphonium bromide. Within the limits of ^1H NMR detection, no complex aldol derivatives were found.[13i] Addition of the bromo ester **7c** to a melt of triphenylphosphine led to a rapid exothermic reaction and resulted in the formation of a dark brown gel comprising of at least five phosphonium salts. In a related study, a melt of triphenylarsine reacted with alkyl 4-bromo-3-oxobutanoates **7a** and **7b** to give the corresponding pure arsonium salts.[16]

The corresponding alkyl 4-chloro-3-oxobutanoates **7e** and **7f** reacted with triphenylphosphine either in toluene or when the substrates were added neat and heated in an oven for 2 h at 80 °C. Impure (3-alkoxycarbonyl-2-oxopropyl)triphenylphosphonium chlorides **8e** and **8f** were isolated (Scheme 3). A mixture of chlorinated phosphonium salts were by-products and very little alkyl 3-oxobutanoate **6a** and **6b** could be found in the reaction mixture.

Protection of alkyl 4-halo-3-oxobutanoates 7

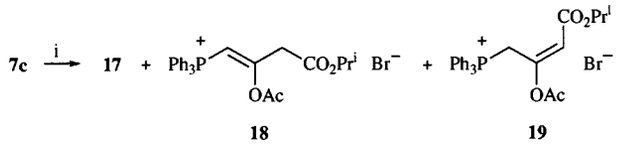
To eliminate the formation of undesirable by-products during the reaction of alkyl 4-halo-3-oxobutanoate **7** with triphenylphosphine, a new route was investigated, involving protection of the keto group of the haloketo ester **7** followed by reaction with triphenylphosphine and subsequent cleavage of the protected keto group. Protection of the keto group of **7c** as a ketal was accomplished with glycol and *p*-TsOH as a catalyst and gave isopropyl 2-bromomethyl-1,3-dioxolane-2-ethanoate **15**. Unfortunately, the 2-bromomethyl-1,3-dioxolane **15** failed to react with triphenylphosphine. Instead the bromo ester **7c** was refluxed with excess isopropenyl acetate in the presence of *p*-TsOH and gave the *Z*-bromoenol acetate **16c**.[12] Triphenylphosphine and the bromoenol acetate **16c** were heated at 80 °C without solvent for 1 h to give the *Z*-phosphonium salt **17** in almost quantitative yield (Scheme 5). For this quaternisation, it



Scheme 5 *Reagents and conditions:* i, Glycol, *p*-TsOH, C_6H_6, 85%; ii, excess isopropenyl acetate, *p*-TsOH, **16c**: 79% **16e**: 94%; iii, Ph_3P, neat, 80 °C, 1 h

was of crucial importance that the enol acetate bromoester **16c** was very pure, otherwise side reactions seem to take over and generate HBr and acetic acid, resulting in impure phosphonium bromide **17**. With the chloroenol acetates **16e** and **16f** this is even more pronounced. Thus, it was found that although the chloroenol acetates, **16e** and **16f**, were easier to prepare in higher purity than the corresponding bromoenol acetate **16c**, these reacted more slowly at 80 °C with triphenylphosphine to give a foaming brownish black gel and acetic acid.

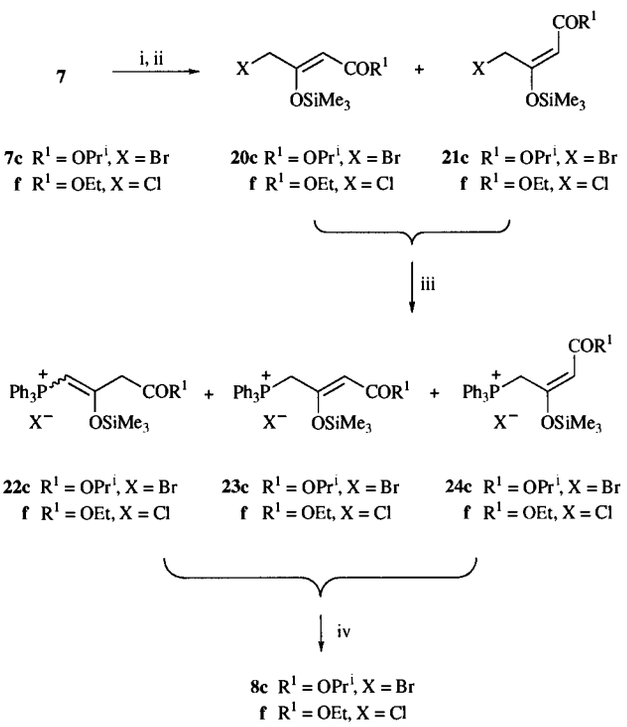
In solution the phosphonium salt **17** rearranged to a mixture of **17**, the *E*-isomer **18** and the vinylic salt **19**. For example, in $CDCl_3$, water-catalysed isomerisation occurred within minutes, while in 'anhydrous' $CDCl_3$ equilibration to the allylic salts **17** and **19** and vinylic salt **18** occurred more slowly, taking seven days to stabilise to a ratio of 25:55:20 (Scheme 6). When



Scheme 6 *Reagents and conditions:* i, Ph_3P in $CDCl_3$, 7 days

kept dry the phosphonium salt **17** was stable. Unfortunately, deprotection of either pure **17** or the mixture of enol acetate phosphonium salts **17**, **18** and **19** in propan-2-ol in the presence of freshly prepared $NaOPr^i$ gave the desired phosphonium ylide **1c**, though rather impure and in only a moderate yield.

Better results were obtained by changing the enol acetate protecting group of alkyl halo-3-oxobutanoates **7** for the trimethylsilyl enol ether group.[17] Deprotonation of isopropyl 4-bromo-3-oxobutanoate **7c** with sodium hydride in diethyl ether at 0 °C, followed by quenching of the anion with trimethylsilyl chloride at room temperature, gave predominantly the *Z*-silyl enol ether **20c** and the *E*-isomer **21c** in a ratio of 13:1 (Scheme 7). The deshielding effect of the ester carbonyl on the methylene

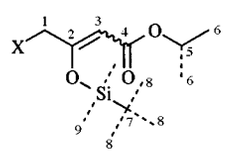


Scheme 7 *Reactions and conditions:* i, NaH, Et_2O; ii, Me_3SiCl; iii, Ph_3P, toluene; iv, few droplets water, toluene

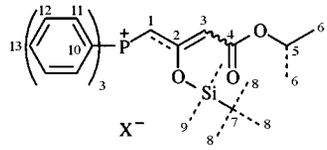
protons of the *E*-isomer **21c** made the assignment possible.[18] It was necessary to use 15% excess sodium hydride and trimethylsilyl chloride. The workup procedure was carried out under strict anhydrous conditions. After the reaction had completed, the suspension was not filtered. Instead the solvent was removed under vacuum and **20c** was directly vacuum distilled and stored under argon.

The reaction of the mixture of silyl enol ethers **20c** and **21c** with triphenylphosphine in toluene at room temperature for 24 h followed by decomposition with a little water, gave exceptionally pure phosphonium bromide **8c** in high yield. This reaction was studied by ^1H NMR spectroscopy. Treatment of silyl enol ether **20c** and **21c** with Ph_3P in anhydrous $CDCl_3$ gave a mixture of vinylic- and allylic-phosphonium salts **22c**, **23c** and **24c** (Scheme 7). In a closed NMR-tube, hydrolyses to the phosphonium bromide **8c** took place very slowly. On the other hand, with a little water, hydrolyses to the phosphonium bromide **8c** occurred instantaneously. Likewise, the trimethylsilyl enol ethers **20f** and **21f** were produced from ethyl chloro-3-

Table 2 ^{13}C Chemical shifts (δ_C in ppm) of compounds **20c**, **20f**, **21f**, **26c**, **22c**, **24c** and **28c**[a,b]



20c X = Br
21c X = Br
20f X = Cl
21f X = Cl
25c X = Br
25f X = Cl
26f X = Cl



22c X = Br
24c X = Br
27c X = Br
28c X = Br

					22c 62–58%		**24c** 38–42%		**28c** 79%	
C	**20c**	**20f**	**21f**	**25c**		J_{PC}		J_{PC}		J_{PC}
1	33.77	46.16	40.96	28.81	83.34	94.4	~27[c]	~55[c]	29.24	49.7
2	160.34	160.38	164.61	165.49	157.48	10.7	164.28	2.5	159.05	10.9
3	102.53	101.99	101.51	102.04	41.60	13.0	101.11	*d*	104.46	*d*
4	164.36	164.86	166.30	166.58	168.35	3.6	165.64	*d*	165.87	2.9
5	66.62	59.51	59.83	67.67	67.56		65.56		67.25	
6	21.93	14.28	14.12	22.42	19.93		19.9		21.30	
7	0.66	0.52	−0.14	18.00	−1.47		−2.16		17.44	
8				25.90					24.84	
9				−4.34					−5.13	
10					118.38	91.8	116.18	81.80	117.28	87.2
11					131.30	10.8	131.99	10.4	133.60	10.3
12					128.24	13.0	128.17	12.9	129.77	13.0
13					132.68	3.0	133.21	2.8	134.79	3.0

[a] At 50.3 MHz in $CDCl_3$ and J_{PC} measured in Hz. [b] Consult Schemes 7 and 8 for compounds. [c] δ_C and J_{PC} not accurate. [d] J_{PC} too small to be measured.

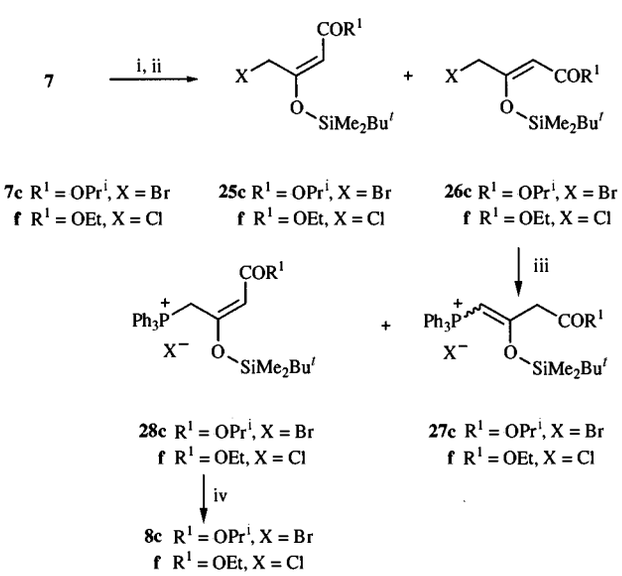
Table 3 ^{1}H Chemical shifts (δ_H in ppm) of compounds **20c**, **21c**, **20f**, **21f**, **25c**, **26c**, **25f**, **26f**, **22c**, **24c**, **22f**, **24f**, **27c** and **28c**[a,b]

								22c 62–58%		**24c** 38–42%		**27c** 21%		**28c** 79%	
H	**20c**	**21c**	**20f**	**21f**	**25c**	**25f**	**26f**		J_{PH}		J_{PH}		J_{PH}		J_{PH}
1	3.79	4.48	3.90	4.60	4.47	4.55	3.84	6.53	18.0	5.77	15.8	6.15	~14[c]	5.47	15.9
3	5.37	5.14	5.41	5.20	5.12	5.12	5.36	4.07	1.9	5.08	*b*	4.00	~2[c]	5.08	3.6
5	5.03	5.03	4.15	4.16	5.03	4.09		5.07		4.82				4.77	
6	1.24	1.26	1.27	1.28	1.24	1.21		1.30		1.14				1.09	
7	0.33	0.32	0.32	0.32				−0.070		0.125					
8					0.96	0.91								0.72	
9					0.27	0.21								0.18	
Ph								7.95–7.75		7.95–7.75		7.88–7.64		7.88–7.64	

[a] At 200 MHz in $CDCl_3$ and J_{PH} measured in Hz. [b] J_{PH} too small for accurate measurements. [c] Data not accurate.

oxobutanoate **7f** in the ratio of 7:1 following the same procedure. However, reaction of this mixture of **20f** and **21f** with Ph_3P in $CDCl_3$ at room temperature led to isomerisation to the thermodynamically more stable silyl enol ether **21f**. In $CDCl_3$ at 60 °C slow quaternisation gave impure phosphonium salt **22f** and substantial desilylation took place.

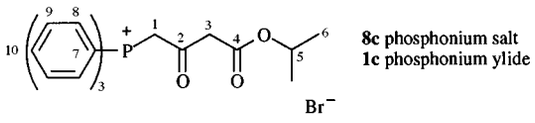
Instead of trimethylsilyl enol ethers **20** and **21**, the more stable *tert*-butyldimethylsilyl enol ethers **25** and **26** were prepared from alkyl 4-bromo-3-oxobutanoate **7** using the same procedure as for the trimethylsilyl enol ether syntheses. The reactions were performed in anhydrous THF and took considerably longer to complete.[19] The workup of *tert*-butyldimethylsilyl enol ethers **25** and the minor *Z*-isomers **26** respectively, was carried out by a simple filtration through silica gel. In this case no deprotection took place and the silyl enol ethers **25c**, **26c** and **25f**, **26f** were far less sensitive to moisture. Reaction of a mixture of *tert*-butyldimethylsilyl enol ethers **25c** and **26c** with Ph_3P in toluene gave a mixture of vinylic phosphonium bromide **27c** and allylic phosphonium bromide **28c** in high yield (Scheme 8). Deprotection of these silyl enol ether phosphonium salts **27c** and **28c** was successfully carried out by adding a little water and filtering the precipitate. A high yield of pure phosphonium bromide **8c** was thus obtained without the aid of a deprotection reagent.[20] The mixture of **25f** and **26f** was heated with Ph_3P without any solvent, but unfortunately this led to deprotection. An impure mixture of phosphonium salts **27f** and **28f** was obtained together with *tert*-butyldimethylsilyl chloride, *tert*-butyldimethylsilanol and bis(*tert*-butyldimethylsilyl) ether. This complex mixture was dissolved in dichloromethane and treated with a little water. Precipitation with toluene and recrystallisation gave a fairly pure sample of the phosphonium salt **8f**.



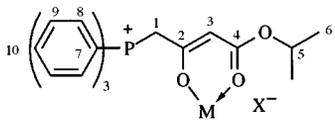
Scheme 8 *Reactions and conditions:* i, NaH, THF; ii, Bu^{t}Me$_2$SiCl; iii, Ph_3P, toluene; iv, few droplets water, toluene

The phosphonium ylide **1c** was prepared by treating a dichloromethane solution of the corresponding phosphonium

Table 4 ^{13}C Chemical shifts (δ_C in ppm) of compounds **1c**, **1c** (solid state), **8c**, **29a**, **29b**, **30**[a]



8c phosphonium salt
1c phosphonium ylide



29a M = Zn, X = Br
b M = Zn, X = Cl
30 M = Li, X = I

			1c								**30**			
	8c		Solution		Solid		**29a**		**29b**		64%		36%	
C		J_{PC}		J_{PC}	Keto	Enol[b]		J_{PC}		J_{PC}		J_{PC}		J_{PC}
1	40.86	58.2	52.26	109	52.7	46.5	36.54	53	36.44	52.9	65.15	41.5	45.92	17.3
2	196.66	7.1	183.99	2.2	184.3	169.7	174.07	6.8	174.23	6.7	174.17	*c*	182.75	*c*
3	50.74	6	48.61	15.1	48.4	93.8	88.86	5.5	88.90	7.5	90.63	5.1	62.71	2.6
4	167.36	*d*	170.13	*d*	170.9	170.9	172.59	*d*	172.70	0	172.70	0	172.70	0
5	69.93		67.47		67.5	70.1	67.72		67.66		65.56		69.69	
6	22.18		21.73		21.7/21.9	20.7	21.58		21.57		21.84		21.47	
7	118.75	88.9	126.41	90.9	126.8	124.7	118.10	87.8	118.17	87.8	118.00	86.9	123.31	91.3
8	134.24	10.8	132.96	10.2	132.3	*c*	133.72	10.2	133.71	10.2	133.89	10.1	132.97	10.4
9	130.67	13.1	128.73	12.3	127.7	125.6	129.93	12.9	129.91	12.9	130.06	12.8	129.55	12.6
10	135.37	2.8	132.01	*d*	131.0	*c*	134.61	*d*	134.59	3	134.60	*d*	132.96	*d*

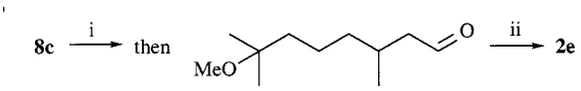
[a] At 50.3 MHz in $CDCl_3$ and J_{PC} measured in Hz. [b] δ_C of the enol tautomer should be taken with caution. [c] Not observed. [d] J_{PC} too small to be measured.

Table 5 ^{1}H Chemical shifts (δ_H in ppm) of compounds **1c**, **8c**, **29a**, **29b**, **30**[a]

	8c		**1c**		**29a**		**29b**		**30**			
H		J_{PH}		J_{PH}		J_{PH}		J_{PH}	Major	J_{PH}	Minor	J_{PH}
1	6.17	11.3	3.832	23	4.102	14.1	4.116	14.2	4.268	14.9	4.116	21.3
3	4.095	2.6	3.325	1.3	4.744	0	4.743	0	4.305	0	3.569	0
5	4.994		5.066		4.929		4.923		4.55		4.647	
6	1.22		1.256		1.096		1.091		0.973		1.13	
Ph	7.89–7.58		7.7–7.4		7.80–7.53		7.70–7.55		7.74–7.59		7.74–7.59	

[a] At 200 MHz in $CDCl_3$ and J_{PH} measured in Hz.

Table 6

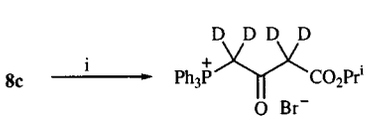


		Yield (%)		
Run	*Reagents and conditions*	Keto ester **2e**	Ratio *Z*:*E*	Residue[a]
1	i, CH_2Cl_2, Zn, 40 °C, 48 h, workup; ii, THF, 0 °C, $KOBu^t$, 12 h	10	3:7	
2	i, aq. NaOH, CH_2Cl_2, 30 min, workup; ii, CH_2Cl_2, RT,[b] 36 h, 38 °C, 15 h	7	1:99	61
3	i, THF, 2 equiv. $KOBu^t$, 0 °C, 30 min; ii, THF, 0 °C, 15 min	25	96:4	12

[a] Complex condensation products. Note that complex phosphonium compounds may form during condensations with **1**.[22] [b] RT = room temperature.

salt **7c**, with aqueous sodium carbonate. The ambident nucleophilic nature of alkyl 3-oxo-4-(triphenylphosphoranylidene)-butanoate **1** has been demonstrated,[5,7–10] and this was shown by the following experiments. ^{1}H and ^{13}C NMR spectroscopy of **8c** in $CDCl_3$ showed no enolisation. Addition of a little D_2O led to deuterium exchange of both the α- and the γ-protons at an equal rate which clearly shows that deprotonation of **8c** can occur at both the α-methylene and the γ-methylene positions. Excess D_2O deuteriated all four methylene protons within 5 min (Scheme 9). Deuterium exchange in the phosphonium ylide **1c** in $CDCl_3$ showed a similar result; all three positions were deuteriated within 5 min.

The phosphonium salt **8c** reacted like a typical ambidentate

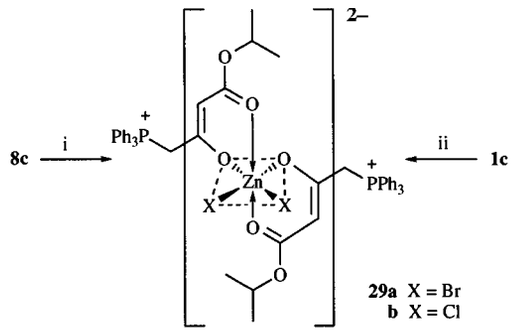


Scheme 9 *Reagents and conditions:* i, in $CDCl_3$ add excess D_2O

complexing reagent; a solution of **8c** in $CDCl_3$ dissolved zinc, liberating hydrogen to form the complex **29a**.[21] Alternatively, the ylide **1c** complexed with $ZnCl_2$ to form the equivalent chloro complex **29b** (Scheme 10). ^{1}H and ^{13}C NMR studies showed the differences in chemical shifts between the complexes formed from LiI and the ylide **1c** in $CDCl_3$, and those complexes obtained from **1c** and Lewis acids like $ZnCl_2$, $AlCl_3$ and $SnCl_4$ in $CDCl_3$ (Tables 4 and 5).†

An investigation of whether metal enolates like **29a** and **29b** could be used as Wittig reagents in condensations with aldehydes was conducted (Table 6, run 1), and compared with the conventional Wittig condensations of **1c** (Table 6, run 2). However, no advantage with this procedure was observed.

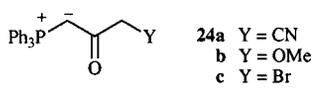
† *Supplementary data:* Experimental procedures and spectrometric data for compounds **1d**, **6c**, **6d**, **7c**, **7d**, **7f**, **8d**, **15**, **16c**, **16e** and metal enolates **30** (M = Al, X = Cl), and **30** (M = Sn, X = Cl) are available as supplementary data (no. 57243). Contact the British Library for details. For further information on the Supplementary Publications scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1.



Scheme 10 *Reagents and conditions:* i, Zn in $CDCl_3$ or CH_2Cl_2; ii, $ZnCl_2$·dioxane complex in $CDCl_3$

Conclusion

Preparation of trimethylsilyl enol ethers of alkyl 4-bromo-3-oxobutanoates **7a**–**7c**, followed consecutively by treatment of triphenylphosphine and a little water in toluene, gave pure (3-alkoxycarbonyl-2-oxopropyl)triphenylphosphonium bromides **8a**–**8c**. The same protocol did not work with alkyl 4-chloro-3-oxobutanoates **7e** and **7f**. However, protection of the carbonyl group as *tert*-butyldimethylsilyl enol ethers followed consecutively by quaternisation with Ph_3P and a little water in toluene gave the corresponding fairly pure phosphonium chlorides **8e**–**8f**. This preparative procedure can be extended to a range of other β,δ-substituted phosphonium salts like **8g**[1] and **8h**–**8j**[4c] (Scheme 3), which were otherwise obtained in a rather modest yield of 48–60%[4c] of the isolated corresponding ylides and also the phosphonium ylides **24** (Scheme 11).[23] Deuterium



Scheme 11

exchange of the phosphonium salt **8c** and the formation of metal enolates of (3-isopropoxycarbonyl-2-oxopropyl)triphenylphosphonium bromide **8c** are indicative of the ambident nucleophilic behaviour of isopropyl 3-oxo-4-(triphenylphosphoranylidene)butanoate **1c**.

Experimental

^{1}H NMR (δ, ppm, with $SiMe_4$ as an internal standard) and ^{13}C NMR spectra (δ, ppm) were recorded in $CDCl_3$ on a Varian Gemini-200 spectrometer at 200 and 50.3 MHz respectively. ^{31}P NMR spectra were obtained on a Bruker AM-300 instrument at 121.5 MHz and referenced to an external standard of 85% H_3PO_4. *J* Values are given in Hz. High resolution chemical ionisation spectra (CI) using ammonia and liquid secondary ion mass spectra (LSIMS) were obtained from a Kratos Concept ISQ instrument. Infrared spectra were obtained on a Hitachi 270-30 FTIR spectrophotometer (film, NaCl plates). Ultraviolet absorbance was measured as solutions in 96% EtOH on a Shimadzu UV-150 spectrophotometer. Microanalyses were obtained using a Carlo Erba, CHNSO EA 1108 Elemental Analyser. Column chromatography was performed using Merck Si-60 (40–63 mm) silica gel. Methyl 3-oxobutanoate **6a**, ethyl 3-oxobutanoate **6b**, methyl 4-chloro-3-oxobutanoate **7e** and ethyl 4-chloro-3-oxobutanoate **7f** were obtained from Aldrich Chemical Co. and distilled before use. Methyl 4-bromo-3-oxobutanoate **7a** was prepared according to the literature.[12] Trimethylsilyl chloride was obtained from Aldrich Chemical Co. and used without further purification. *tert*-Butyldimethylsilyl chloride was obtained from Aldrich Chemical Co. and sublimed before use.†

Reaction of isopropyl 4-bromo-3-oxobutanoate 7c and Ph_3P in different solvents

Method (1). Isopropyl 4-bromo-3-oxobutanoate **7c** (0.43 g, 1.927 mmol; 1% excess) in anhydrous solvent (0.5 cm^3) was added to a solution of triphenylphosphine (0.50 g, 1.906 mmol) in the same solvent (2, 3 or 5 cm^3, depending on solubility) within 1 min at room temperature and stirred for 24 h. First, the clear solvent phase was analysed by ^{1}H NMR spectroscopy. Then the solvent was removed from the reaction mixture and the entire homogeneous residue was analysed by ^{1}H NMR and ^{13}C NMR spectroscopy to obtain the ratios of (3-isopropoxycarbonyl-2-oxopropyl)triphenylphosphonium bromide **8c**, isopropyl 4-bromo-3-oxobutanoate **7c**, isopropyl 3-oxobutanoate **6c** and other phosphonium salts (see Table 1).†

Method (2). Slow addition of portions of triphenylphosphine to a solution of isopropyl 4-bromo-3-oxobutanoate **7c** in $CDCl_3$ at room temperature led to a 60.5% yield of **8c** [based on the ^{1}H NMR integration of the methylene (1-H_2) doubled (δ_H 6.18, J_{PH} 11.5) and the isopropoxy methyl groups at δ_H 1.22] and 18% of **6c** [isopropoxy methyl groups at δ_H 1.27 and the methyl group (4-H_3) at δ_H 2.28]. The region between δ_H 7.9 and 7.5 showed a 21–28% excess due to Ph_3P=O and what we assume to be $Ph_3P^+OH\ Br^-$. Three other phosphonium salts had isopropoxy methyl doublets at δ_H 1.08 (9.3%), 0.89 (3.4%) and 0.81 (1.9%) and a further 6.6% material was unaccounted for. Typical phosphorus coupling doublet of doublets and doublets were seen at δ_H 6.50 (dd, J_{PH} 21 and J_{HH} 5) and 5.19 (d, J_{PH} 15.7). **9c**: [Found: M^+(LSIMS), 483.0755. $C_{25}H_{25}BrO_3P$ requires *M*, 483.0725]. **10c**: [Found: M^+(LSIMS), 467.0785. $C_{25}H_{25}BrO_2P$ requires *M*, 467.0776] (see Scheme 4).†

(3-Isopropoxycarbonyl-2-oxopropyl)triphenylphosphonium bromide 8c

Isopropyl 4-bromo-3-oxobutanoate **7c** (50.0 g, 0.224 mol) in anhydrous benzene (100 cm^3) was added to triphenylphosphine (59.5 g, 0.227 mol) in anhydrous benzene (300 cm^3) at room temperature and stirred for 24 h. The precipitate was recrystallised from propan-2-ol (200 cm^3) and benzene (400 cm^3) to give clear white crystals of (3-isopropoxycarbonyl-2-oxopropyl)-triphenylphosphonium bromide **8c** which were filtered and dried (90.1 g, 82.9%) (Found: C, 61.8; H, 5.5. $C_{25}H_{26}BrO_3P$ requires C, 61.9; H, 5.4%); ν_{max}(KBr)/cm^{-1} 3490 (br m), 3415 (br m), 3040 (w), 2970 (m), 2770 (br m), 1739 (vs), 1715 (s), 1438 (s), 1352 (s), 1338 (s), 1283 (m), 1210 (m), 1124 (m), 1105 (s), 967 (m), 749 (s), 717 (m), 691 (s); δ_P($CDCl_3$, 20 °C) 18.68 [Found: M^+(LSIMS), 405.1634. $C_{25}H_{26}O_3P$ requires *M*, 405.1620); *m/z* (LSIMS) 405 (M^+, 100%), 345 (20), 319 (30), 275 (12), 183 (17).

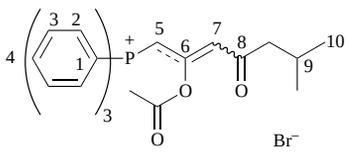
Isopropyl 3-oxo-4-(triphenylphosphoranylidene)butanoate 1c

A solution of sodium carbonate (22.0 g, 0.208 mol) in water (600 cm^3) was added to a solution of (3-isopropoxycarbonyl-2-oxopropyl)triphenylphosphonium bromide **8c** (95.1 g, 0.1959 mol) in dichloromethane (500 cm^3) within 20 min under vigorous stirring and stirred for another 3 h. The organic phase was separated, washed with water and dried ($MgSO_4$), the solvent was evaporated and the crude phosphonium ylide recrystallised from benzene to give isopropyl 3-oxo-4-(triphenylphosphoranylidene)butanoate **1c** (67.8 g, 85.6%) (Found: C, 74.2; H, 6.2. $C_{25}H_{25}PO_3$ requires C, 74.4; H, 6.3%); ν_{max}(mull, CH_2Cl_2)/cm^{-1} 3020 (w), 2980 (w), 1719 (s), 1576 (m), 1555 (s), 1436 (m), 1390 (s), 1313 (m), 1178 (m), 1106 (s), 864 (m), 750 (m), 717 (m), 695 (m) [Found: M^+(LSIMS), 404.1525. $C_{25}H_{25}O_3P$ requires *M*, 404.1541]; *m/z* (LSIMS) 405 (MH^+, 100%), 303 (40), 279 (10), 145 (10); *m/z* (CI) 405 (100%), 345 (20), 319 (30), 275 (12), 183 (17).

(2-Acetoxy-3-isopropoxycarbonylprop-2-enyl)triphenylphosphonium bromide 17

Isopropyl 3-acetoxy-4-bromobut-2-enoate **16c** (205 mg, 0.773 mmol) in $CDCl_3$ was treated with triphenylphosphine (215 mg,

Table 7 ^{13}C Chemical shifts (δ_C in ppm) of compounds **17** (allyl, *Z*), **19** (allyl *E*) and **18** (vinyl)[a]



No.	17	19	18
1	116.72 (87.0)	116.90 (86.7)	118.60 (92.0)
2	133.73 (10.3)	133.94 (10.3)	133.36 (11.1)
3	129.80 (12.9)	130.08 (12.9)	130.28 (13.3)
4	134.86 (2.8)	135.68 (3.0)	134.90 (3.0)
5	30.84 (50.9)	27.81 (50.7)	96.89 (88.6)
6	148.12 (12.1)	152.17 (11.8)	165.80 (20.2)
7	116.06 (10.2)	~115.3 (11)	40.77 (11.5)
8	161.87 (2.5)	~164.5	166.38
9	67.44	68.52	69.22
10	21.2	21.52	21.52
11	166.55	166.34	166.94
12	19.87	20.94	19.69

[a] At 50 MHz in $CDCl_3$ with J_{PC} measured in Hz in parentheses.

Table 8 ^{1}H Chemical shifts (δ_H in ppm) of compounds **17**, **19** and **18**[a]

No.	17	19	18
Ph	7.95–7.67	7.95–7.67	7.95–7.67
5	5.35 (15.4)	obscured ~5.1	5.57 (16.1)
7	6.48 (3.9)	6.03 (4.5)	4.28
9	4.91 (6.2)	4.69 (6.2)	5.01 (6.2)
10	1.16 (6.2)	1.07 (6.2)	1.24 (6.2)
12	1.70	1.91	1.42

[a] At 200 MHz in $CDCl_3$ with J_{PH} measured in Hz in parentheses.

0.81 mmol) and left to stand for 7 days. The solution turned yellow after 24 h. After 7 days the reaction was complete and had equilibrated to a mixture of (*E*)- and (*Z*)-(2-acetoxy-3-isopropoxycarbonylprop-2-enyl)triphenylphosphonium bromide **19** and **17** in 20 and 25% yield respectively and (2-acetoxy-3-isopropoxycarbonylprop-1-enyl)triphenylphosphonium bromide (55%) **18** (Tables 7 and 8).

Macroscale procedure. Isopropyl 3-acetoxy-4-bromobut-2-enoate **16c** (6.00 g, 22.6 mmol) was added to dried triphenylphosphine (6.00 g, 22.9 mmol) and was slowly heated in an oil bath to a melt. The ingredients were thoroughly mixed and kept in an oven at 70 °C. The viscous melt solidified in 15 min and was kept for another 1 h at 70 °C to give an almost quantitative yield of only (*Z*)-(2-acetoxy-3-isopropoxycarbonyl-prop-2-enyl)triphenylphosphonium bromide **17** (Found: C, 61.5; H, 5.35. $C_{27}H_{28}BrO_4P$ requires C, 62.0; H, 5.4%); ν_{max}(film)/cm^{-1} 3045 (m), 2990 (m), 2850 (m), 2750 (m), 1780 (s), 1709 (s), 1657 (m), 1438 (m), 1360 (s), 1235 (s), 1168 (s), 1102 (s), 1012 (m), 994 (m), 758 (m), 719 (m), 691 (s) [Found: M^+(LSIMS), 447.1684. $C_{27}H_{28}O_4P$ requires *M*, 447.1725]; *m/z* (LSIMS) 447 (M^+, 100%), 405 (2), 345 (80), 262 (20), 183 (20).

Isopropyl 4-bromo-3-(trimethylsilyloxy)but-2-enoate 20c

Isopropyl 4-bromo-3-oxobutanoate **7c** (2.00 g, 8.96 mmol) in anhydrous diethyl ether (3 cm^3) was added within 5 min to an oil free suspension of sodium hydride (0.27 g, 11.3 mmol) in anhydrous diethyl ether (20 cm^3) at 0 °C. A vigorous evolution of hydrogen gas resulted and the reaction mixture was stirred for a further 15 min at 0 °C. The reaction mixture was treated with trimethylsilyl chloride (1.40 cm^3, 1.198 g, 11.0 mmol) with vigorous stirring at 0 °C. A gel, formed of finely divided sodium chloride in diethyl ether, was shaken loose before stirring the mixture for another 60 min. The gel suspension was transferred under anhydrous conditions to a small flask and the solvent removed cautiously under vacuum and the powder-gel bulb-to-bulb vacuum distilled to give isopropyl 4-bromo-3-(trimethylsilyloxy)but-2-enoate **20c** (1.20 g, 45.3%); bp 90 °C/0.2 mmHg (Found: C, 40.7; H, 6.5. $C_{10}H_{19}BrO_3Si$ requires C, 40.7; H, 6.7%); ν_{max}(film)/cm^{-1} 2980 (m), 1717 (s), 1632 (s), 1468 (w), 1402 (s), 1386 (s), 1374 (s), 1235 (s), 1207 (s), 1163 (s), 1109 (s), 1016 (s), 998 (m), 848 (s) [Found: M^+(EI), 294.0271. $C_{10}H_{19}BrO_3Si$ requires *M*, 294.0287]; *m/z* (EI) 294 (M^+, 3%), 252 (20), 237 (100), 159 (50), 143 (20), 99 (15), 75 (55), 73 (70).

Preparation of (3-isopropoxycarbonyl-2-oxopropyl)triphenylphosphonium bromide 8c *via* isopropyl 4-bromo-3-(trimethylsilyloxy)but-2-enoate 20c and triphenylphosphine

Isopropyl 4-bromo-3-(trimethylsilyloxy)but-2-enoate **20c** (0.90 sg, 3.43 mmol) was added neat to a solution of triphenylphosphine (0.89 g, 3.39 mmol) in anhydrous toluene (5 cm^3) and stirred for 24 h at room temperature. After 30 min a yellowish white precipitate started to form, and after 24 h the precipitation of a mixture of phosphonium bromides **22c**, **23c** and **24c** was complete. A few droplets of water were added to a fast stirring suspension of the salt and stirred for 3 h. The resulting salt was filtered and dried at 40 °C to give without further purification (3-isopropoxycarbonyl-2-oxopropyl)triphenylphosphonium bromide **8c** (1.55 g, 94.2%) (Found: C, 61.8; H, 5.5. $C_9H_{15}BrO_4$ requires C, 61.9; H, 5.4%). For the mixture **22c**, **23c** and **24c**: [Found: $(MH - SiMe_3)^+$(LSIMS), 405.1612. $C_{25}H_{26}O_3P$ requires $MH - SiMe_3$ 405.1620]; *m/z* (LSIMS) 477 (M^+, 100%), 405 (50), 345 (15), 262 (40) (note the silyl group was too labile for accurate mass determination).

Ethyl 4-chloro-3-(trimethylsilyloxy)but-2-enoate 20f

Ethyl 4-chloro-3-oxobutanoate (2.00 g, 12.15 mmol) in anhydrous diethyl ether (3 cm^3) was added to an oil free suspension of sodium hydride (0.36 g, 15.0 mmol) in anhydrous diethyl ether (20 cm^3) at 0 °C within 5 min. A vigorous evolution of hydrogen gas resulted and the reaction mixture was stirred for a further 15 min at 0 °C. The reaction mixture was quenched, all at once, with trimethylsilyl chloride (1.80 cm^3, 1.54 g, 14.18 mmol) with vigorous stirring at 0 °C. A gel, formed of finely divided sodium chloride in diethyl ether, was shaken loose before stirring for another 60 min. The gel suspension was transferred under anhydrous conditions to a small flask and the solvent removed cautiously under vacuum and the dry powder-gel bulb-to-bulb vacuum distilled to give ethyl 4-chloro-3-(trimethylsilyloxy)but-2-enoate **20f** (2.35 g, 81.7%); bp 70 °C/0.1 mmHg (Found: C, 45.8; H, 7.55. $C_9H_{17}ClO_3Si$ requires C, 45.7; H, 7.2%); ν_{max}(film)/cm^{-1} 2960, 1721 (s), 1636 (s), 1405 (m), 1252 (m), 1214 (s), 1170 (m), 1149 (m), 1046 (m), 999 (m), 849 (s).

Preparation of isopropyl 4-bromo-3-(*tert*-butyldimethylsilyloxy)-but-2-enoate 25c

Isopropyl 4-bromo-3-oxobutanoate **7c** (2.00 g, 8.96 mmol) was added neat (*via* syringe) to a suspension of oil free sodium hydride (0.30 g, 12.5 mmol) in anhydrous THF (20 cm^3) within 5 min at 0 °C with stirring. A vigorous evolution of hydrogen gas resulted, and stirring was continued for another 20 min at 0 °C. The soluble anion was treated with *tert*-butyldimethylsilyl chloride (1.50 g, 9.95 mmol) in anhydrous THF (5 cm^3) within 3 min and stirred for 3 days at room temperature. At 0 °C no precipitation of NaCl occurred, but at room temperature a suspension started to form after 2 h. After the reaction was complete, the solution was diluted with anhydrous diethyl ether (50 cm^3) and filtered over a bed (2 cm) of silica gel. The solvents were removed under reduced pressure, which gave a crude residue (2.78 g, 91.9%), contaminated with NaCl. This residue was bulb-to-bulb distilled to give isopropyl 4-bromo-3-(*tert*-butyldimethylsilyloxy)but-2-enoate **25c** (2.05 g, 67.8%) (bp 125 °C/0.5 mmHg) which solidified in the refrigerator at −21 °C (Found:

C, 46.1; H, 7.75. $C_{13}H_{25}BrO_3Si$ requires C, 46.3; H, 7.5%); ν_{max}(film)/cm^{-1} 2978 (m), 2956 (m), 2935 (s), 2860 (m), 1716 (s), 1706 (s), 1700 (s), 1626 (s), 1616 (s), 1472 (m), 1465 (m), 1420 (m), 1372 (m), 1329 (s), 1306 (s), 1256 (s), 1161 (s), 1154 (s), 1128 (s), 1110 (s), 1032 (s), 933 (m), 906 (m), 842 (s), 834 (s), 826 (s); λ_{max}(EtOH)/nm 205, 247 (ε/dm^3 mol^{-1} cm^{-1} 3300, 9050) [Found: M^+(LSIMS), 337.0822. $C_{13}H_{26}BrO_3Si$ requires *M*, 337.0835]; *m/z* (LSIMS) 337 (M^+, 55%), 295 (15), 279 (100), 237 (60), 215 (20).

Preparation of (3-isopropoxycarbonyl-2-oxopropyl)triphenylphosphonium bromide 8c. The reaction of triphenylphosphine and (*E*)-isopropyl 4-bromo-3-(*tert*-butyldimethylsilyloxy)but-2-enoate 25c

(*E*)-Isopropyl 4-bromo-3-(*tert*-butyldimethylsilyloxy)but-2-enoate **25c** (337 mg, 1 mmol) in $CDCl_3$ (0.7 cm^3) was treated with dried triphenylphosphine (268 mg, 1.02 mmol) at room temperature, for 4 h. ^{1}H NMR spectroscopy showed that the phosphonium salt in a mixture of [3-isopropoxycarbonyl-2-(*tert*-butyldimethylsilyloxy)prop-2-enyl]triphenylphosphonium bromide (*E* isomer) **28c** and [3-isopropoxycarbonyl-2-(*tert*-butyldimethylsilyloxy)prop-1-enyl]triphenylphosphonium bromide **27c** had formed. The deuteriochloroform solution was added within 5 min to toluene (10 cm^3) and then treated with 2 drops of water and vigorously stirred for 2 h at room temperature. The precipitate was filtered and washed with toluene to give, after drying, pure [3-isopropoxycarbonyl-2-oxopropyl]-triphenylphosphonium bromide **8c** (0.41 g, 84.5%).

Preparation of ethyl 3-(*tert*-butyldimethylsilyloxy)-4-chlorobut-2-enoate 25f

Ethyl 4-chloro-3-oxobutanoate **7f** (2.00 g, 12.15 mmol) was added neat (*via* syringe) to a suspension of oil free sodium hydride (0.36 g, 15.0 mmol) in anhydrous THF (20 cm^3) within 5 min at 0 °C. The reaction mixture was stirred magnetically and a vigorous evolution of hydrogen gas resulted. The reaction mixture was stirred for another 20 min at 0 °C, before the resulting pale yellow, soluble anion was treated with *tert*-butyldimethylsilyl chloride (2.00 g, 13.27 mmol) in anhydrous THF (5 cm^3) within 5 min and stirred for 3 days at room temperature. At room temperature a suspension was formed after 2 h. After the reaction had completed the solution was diluted with anhydrous diethyl ether (50 cm^3) and filtered over a bed (2 cm) of silica gel. The solvents were removed under reduced pressure and gave a crude residue (3.68 g), contaminated with NaCl. This residue was bulb-to-bulb distilled to give (*E*)-ethyl 4-chloro-3-(*tert*-butyldimethylsilyloxy)but-2-enoate **25f** (2.59 g, 76.4%), bp 105 °C/0.5 mmHg which solidified in the refrigerator at −21 °C (Found: C, 51.7; H, 8.4. $C_{12}H_{23}ClO_3Si$ requires C, 51.7; H, 8.3%); ν_{max}(film)/cm^{-1} 2933 (s), 2860 (s), 1714 (s), 1628 (s), 1472 (m), 1465 (m), 1429 (m), 1370 (m), 1345 (s), 1258 (s), 1167 (s), 1136 (vs), 1047 (m), 902 (m), 842 (m) [Found: M^+(LSIMS), 279.1186. $C_{12}H_{24}ClO_3Si$ requires *M*, 279.1183]; *m/z* (EI) 279 (M^+, 100%), 233 (70), 221 (65), 193 (45).

Preparation of (3-ethoxycarbonyl-2-oxopropyl)triphenylphosphonium chloride 8f. The reaction of triphenylphosphine and (*E*)-ethyl 3-(*tert*-butyldimethylsilyloxy)-4-chlorobut-2-enoate 25f

Method (a). (*E*)-Ethyl 3-(*tert*-butyldimethylsilyloxy)-4-chlorobut-2-enoate **25f** (279 mg, 1 mmol) in $CDCl_3$ (0.7 cm^3) was treated with dried triphenylphosphine (265 mg, 1.01 mmol) at room temperature and was thoroughly mixed and heated at 60 °C for 14 h. After 5 min, the solution became orange. ^{1}H NMR spectroscopy showed that the phosphonium salt in a mixture of [3-ethoxycarbonyl-2-(*tert*-butyldimethylsilyloxy)-prop-2-enyl]triphenylphosphonium chloride (*E* isomer) **28f** and [3-ethoxycarbonyl-2-(*tert*-butyldimethylsilyloxy)-prop-1-enyl]triphenylphosphonium chloride **27f** had formed. The deuteriochloroform solution was added within 5 min to toluene (10 cm^3) and then treated with 2 drops of water and vigorously stirred for 2 h at room temperature. The clear solution was decanted and the sticky residue dissolved in ethanol (1 cm^3) and precipitated with toluene to give after filtration and drying (3-ethoxycarbonyl-2-oxopropyl)triphenylphosphonium chloride **8f** (0.35 g, 81.4%). For mixture **27f** and **28f** intermediates: [Found: M^+(LSIMS), 505.2341. $C_{30}H_{38}O_3PSi$ requires *M*, 505.2328]; *m/z* (LSIMS) 505 (M^+, 75%), 391 (OH-form) (100), 345 (10), 303 (25), 262 (30).

Method (b). (*E*)-Ethyl 3-(*tert*-butyldimethylsilyloxy)-4-chlorobut-2-enoate **25f** (279 mg, 1 mmol) and triphenylphosphine (267 mg, 1.01 mmol) were thoroughly mixed and heated at 60 °C for 5 h. A solid crystallised and a viscous liquid drifted on the top. The liquid was analysed by GC–MS and found to be a mixture of *tert*-butyldimethylsilylchloride, *tert*-butyldimethylsilanol and bis(*tert*-butyldimethylsilyl)ether. $[(CH_3)_3C](CH_3)_2SiCl$: *m/z* (EI) 150 (M^+, 30%), 95 (85), 93 (100), 89 (85), 73 (35); $[(CH_3)_3C](CH_3)_2SiOH$: *m/z* (EI) 132 (M^+, 15%), 75 (100); $[(CH_3)_3C](CH_3)_2SiOSi(CH_3)_2[C(CH_3)_3]$: *m/z* (EI) 246 ($M^+$, 2%), 231 (10), 189 (85), 149 (60), 148 (80), 147 (100), 133 (40), 131 (30), 117 (30), 73 (75).

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