Synthesis and Pyrolytic and Kinetic Behaviour of β,δ′-Dioxo-Stabilised Phosphorus Ylides: Convenient Preparation of γ,δ-Alkynyl Ketones and 2,3-Functionalised Butadienes

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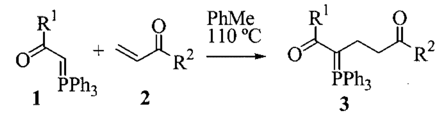
Both ketone- and ester-stabilised phosphorus ylides undergo Michael addition to vinyl ketones to give the β,δ′-dioxo ylides **3** and **5**, respectively, although in the latter case careful temperature control is required to avoid an undesired side-reaction. Under conditions of flash vacuum pyrolysis at 650 °C the ylides **3** generally undergo Ph_3PO extrusion to afford the γ,δ-alkynyl ketones **14**, although these are found to partly undergo a secondary fragmentation. In contrast, the ylides **5** react under the same conditions to give the synthetically useful 1,3-dienes **20** by way of cyclobutenes. Rate constants for the reaction of selected ylides **3** and **5** are reported.

Introduction

In recent papers one of us has shown that thermal extrusion of Ph_3PO from a variety of (β-oxoalkylidene)triphenylphosphoranes using the technique of flash vacuum pyrolysis (FVP) provides a useful synthetic method for functionalised alkynes and various related products.[1,2] In an attempt to extend this chemistry, we have examined the pyrolysis of several new types of stabilised ylides and in this paper we describe the Michael addition of ketone- and ester-stabilised ylides to vinyl ketones to give β,δ′-dioxo ylides[3] and their subsequent pyrolytic behaviour.[4]

Results and Discussion

When ketone-stabilised ylides **1** were treated with vinyl ketones **2** in boiling toluene for 48 h, the expected dioxo ylides **3a**−**g** were formed in good yield as stable solids with ^{31}P NMR signals in the range δ = +16.4 to 18.1 (Scheme 1, Table 1). As we have previously found for other ylide classes, the ^{13}C NMR spectra of these compounds are highly informative, with phosphorus coupling extending throughout the *P*-phenyl groups and to the first carbon atom of R^1 (Table 6, Exp. Sect.). The X-ray structure of compound **3b** has been determined and reported elsewhere.[5]



Scheme 1

Table 1. Reaction of ylides **1** with vinyl ketones **2** to give ylides **3**

Product	R^1	R^2	Yield (%)	M.p. [°C]	δ_P
3a	Me	Me	76	158	18.1
3b	Me	Et	85	148	17.5
3c	Me	$4-MeOC_6H_4$	78	162	18.0
3d	Et	Me	81	111	16.6
3e	Et	Et	83	130	16.4
3f	Ph	Me	89	175	16.6
3g	Ph	Et	80	141	17.4

When the same conditions were applied to the ester-stabilised ylides **4**, the reaction took an unexpected course to give ketone-stabilised ylides **9** together with acrylates **8**. We believe that this can be explained, as shown in Scheme 2, by equilibration of the initial Michael adducts **6**, by way of ring closure to give phosphetanes, with the isomeric intermediates **7** which can then undergo retro-Michael reaction to afford the observed products. The greater thermodynamic stability of **9** as compared to **4** evidently provides the

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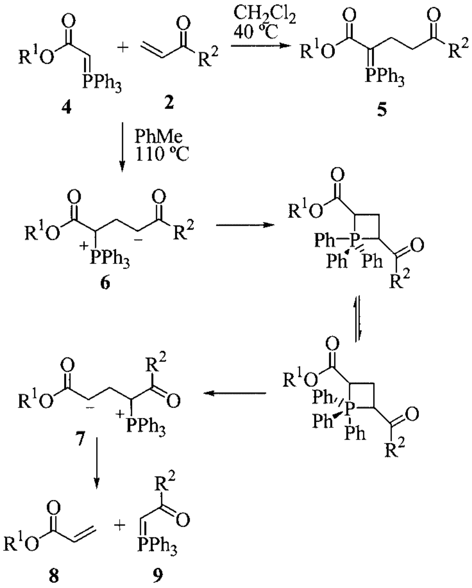
driving force for this process. Fortunately, this problem could be overcome by reducing the reaction temperature, and reaction of **4** with **2** in toluene, or more conveniently CH_2Cl_2, at 40 °C gave the required products **5** in good yield (Scheme 2, Table 2). As one of us has noted previously,[6] ylides of this type may exhibit restricted rotation of the ester group at room temperature leading to separate signals for the (*E*) and (*Z*) isomers in the ^{31}P and ^{13}C NMR spectra of **5a**,**b** and **5d**.

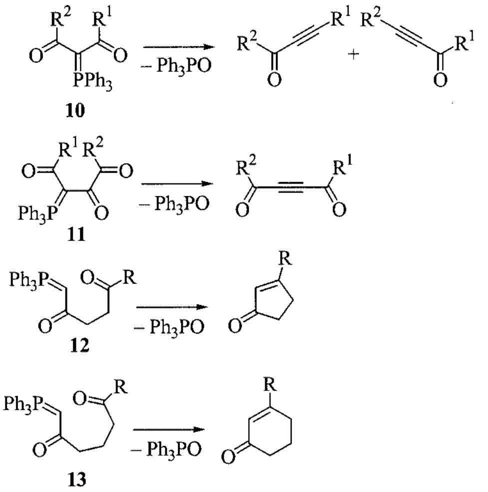


Scheme 2

Table 2. Reaction of ylides **4** with vinyl ketones **2** to give ylides **5**

Product	R¹	R²	Yield (%)	M.p. [°C]	δ_P
5a	Me	Me	91	147	22.0/22.6
5b	Me	Et	92	104	22.8/23.3
5c	Et	Me	87	106	22.5
5d	Et	Et	86	117	22.5/23.6

Previous studies on the pyrolysis of ylides where there is a choice of different carbonyl oxygen atoms available for elimination have shown that while the β,β′-dioxo ylides **10** undergo non-selective elimination to give a mixture of alkynes,[7] the β,γ,β′-trioxo ylides **11** undergo selective elimination across the "central" position to give diacylalkynes in most cases.[8] On the other hand, ylides such as **12** and **13** lose Ph_3PO exclusively between the ylide function and the more remote carbonyl group to give cyclopentenones and cyclohexenones as shown, with no trace of the acetylenic ketones expected from 1,2-elimination.[9]



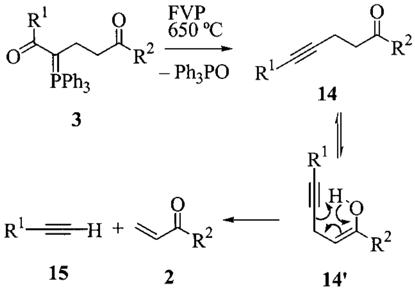
When the ylide **3a** was subjected to FVP at 10^{-2} Torr reaction was found to be incomplete at 500 °C, with some unchanged ylide being recovered. At 650 °C there was complete reaction and the products included the acetylenic ketone **14** expected from 1,2-elimination of Ph_3PO, but this was accompanied by methyl vinyl ketone, and propyne was also present, although its volatility precluded an accurate determination of the yield. It appears that the latter products result from a thermal retro-Michael reaction, perhaps involving the enol form **14′** of the initial product **14** (Scheme 3). Once this pattern had been established, most of the other ylides **3** were found to react in the same way giving the acetylenic ketones **14** in 16−39% yield, accompanied in all cases by the vinyl ketone **2** and terminal alkyne **15** (Table 3).

In the case of **3c** the retro-Michael reaction was complete to give only **2** and **15**. A most unusual and different result was obtained for compound **3d**. In this case Ph_3PO was again obtained together with a single major product which, on the basis of its ^1H and ^{13}C NMR spectroscopic data,

Table 3. Flash vacuum pyrolysis (FVP) of ylides **3**

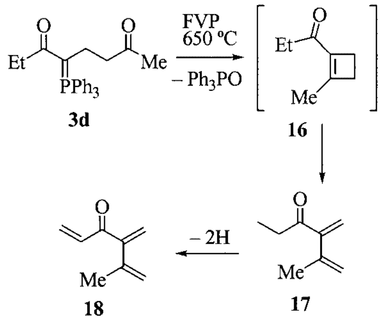
	R¹	R²	Temp. [°C]	Yield of **14** (%)	Yield of **2** (%)	Yield of **15** (%)
3a	Me	Me	650	26	32	+
			500	10	14	+
			750	33	28	+
3b	Me	Et	650	39	49	+
3c	Me	4-$MeOC_6H_4$	650	0	79	+
3d	Et	Me	650	[a]	+	+ (?)
3f	Ph	Me	650	16	29	10
3g	Ph	Et	650	20	36	42

[a] Spectra indicate product to be **18**



Scheme 3

appears to be the triene **18**. Because of its highly reactive nature this product could not be isolated but we are confident the suggested structure is correct because of the excellent agreement of the spectroscopic data with the analogous dienes **20** (see later). Its formation can be explained, as shown in Scheme 4, by postulating Ph$_3$PO elimination between the ylide function and the δ-carbonyl group to give a cyclobutene **16** which might undergo electrocyclic ring-opening to the diene **17** under the conditions used, and this could then lose two hydrogen atoms to give the doubly conjugated ketone triene **18**. It is unclear why this ylide should behave in such a completely different way from the other compounds **3** and this reaction merits further investigation.



Scheme 4

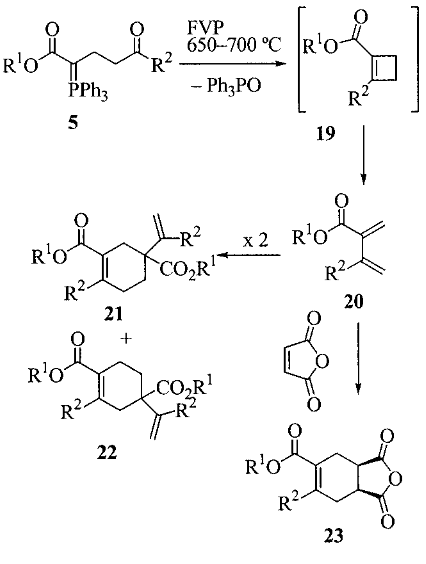
The formation of the acetylenic ketone products **14** by FVP of most of the ylides **3** is a rather useful transformation since it gets around the difficulties normally associated with the Michael addition of a terminal alkyne to an enone. By using the starting ylide **1** as a masked form of the alkyne R^{1}C≡CH we can obtain the same products in two simple steps, although the overall yield is unfortunately low due to the fragmentation to **15** and **2**. The γ,δ-acetylenic ketones **14** have been of considerable recent interest as precursors of substituted furans and pyrroles,[10] and previously reported routes to them include reaction of enones with alkynylboranes,[11] alkynylboranes in the presence of BF$_3$,[12] alkynylstannanes,[13] alkynylaluminium compounds with a nickel catalyst,[14] and alkynes with a rhodium catalyst.[15] Just recently the addition of a chiral binaphthyl-based alkynylboronate has been used to achieve the reaction asymmetrically.[16]

Attention was now turned to the ylides **5** with β-ester and δ-ketone carbonyl groups. As far as we are aware, thermal elimination of Ph$_3$PO between an ylide function and an adjacent ester carbonyl group is unknown. This may be attributed to the fact that such compounds prefer the configuration shown in which the carbonyl group is aligned *anti* to the ylide,[17] although – as noted earlier – both *syn* and *anti* forms could be detected in solution. We have also found previously that a high value of $^2J_{P,CO}$ (≥ 10 Hz) is a reliable indicator for failure of Ph$_3$PO elimination.[8] With values of 12–20 Hz for $^2J_{P,CO}$ compounds **5a–d** therefore appear unlikely to undergo 1,2-elimination. When the ylides **5** were subjected to FVP under the same conditions as for **3** there was again complete extrusion of Ph$_3$PO at 650 °C to give products which were readily identified as the substituted 1,3-dienes **20** (Table 4). A pyrolysis temperature of 700 °C gave slightly higher yields and was routinely used for larger scale reactions.

Table 4. FVP of ylides **5** at 650 or 700 °C

	R^1	R^2	Yield of **20** (%)	Overall yield of **23** (%)
5a	Me	Me	60	32
5b	Me	Et	60	40
5c	Et	Me	50	38
5d	Et	Et	44	30

It seems likely that these products result from elimination of Ph$_3$PO between the ylide function and the ketone carbonyl group to give the cyclobutene intermediates **19** which undergo electrocyclic ring-opening under the conditions used (Scheme 5). As far as we are aware this is the first example of formation of cyclobutenes by an intramolecular Wittig reaction apart from an isolated example reported by Yavari and co-workers while our work was in progress.[18] Despite their rather simple structure, compounds **20a**[19] and **20c**[20] have only been mentioned briefly before, while **20b** and **20d** are previously unknown. Their ^{13}C NMR spectra form a regular pattern which readily confirms the structures (Table 7, Exp. Sect.).



Scheme 5

While the dienes **20** are stable for an extended period in solution, they were observed to dimerise slowly in the pure state, a process accelerated by attempted distillation. The resulting dimers were 1:1 mixtures of two isomers identified as **21** and **22** resulting from reaction of only the electron-poor double bond next to the ester group acting as dienophile but reacting without any regioselectivity. This is the expected pattern of reactivity for 2-(alkoxycarbonyl)butadienes.[21]

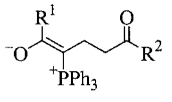
In order to obtain crystalline derivatives for characterisation and at the same time to illustrate the use of the dienes in the Diels−Alder reaction, pyrolyses were carried out on a 1-g scale and the crude products from the cold trap directly reacted with maleic anhydride to give the adducts **23** in reasonable overall yield (Table 4).

Since it has been established that the two types of ylide **3** and **5** both eliminate Ph_3PO but in a quite different way, it was of interest to see whether this was reflected in the kinetics of the reactions. Kinetic studies were performed using a sealed glass tube reactor over the range 410−510 K as detailed in the Exp. Sect. The ylides display first-order kinetics; the resulting rates and Arrhenius parameters are given in Table 8 (Exp. Sect.) and rate constants adjusted to 400 K are shown in Table 5.

Table 5. Kinetic data for ylides **3** and **5**

Compound	R^1	R^2	k [s^{-1}] at 400 K
3a	Me	Me	5.41×10^{-5}
3b	Me	Et	2.14×10^{-5}
3f	Ph	Me	6.02×10^{-8}
3g	Ph	Et	1.66×10^{-7}
5a	Me	Me	7.53×10^{-7}
5b	Me	Et	5.98×10^{-7}
5c	Et	Me	3.97×10^{-6}
5d	Et	Et	1.49×10^{-6}

For the ylides **3** there is a very marked difference of two to three orders of magnitude between the cases where R^1 = Me and R^1 = Ph. Since the key step in the extrusion most likely involves interaction of O^- with P^+ in the resonance form **3′**, this effect is as expected, with the electron-releasing methyl group accelerating the process while the relatively electron-withdrawing phenyl group strongly retards it. When we come to the ylides **5**, the rates are considerably lower than for **3a** and **3b** and do not vary greatly on changing between methyl and ethyl substituents.



3'

Experimental Section

General: M.p.: Reichert hot-stage microscope, uncorrected values. IR: Perkin−Elmer 1420. NMR: Bruker AM300 (300 MHz for ^1H, 75 MHz for ^{13}C), Varian CFT 20 (32 MHz for ^{31}P); all spectra, $CDCl_3$ as solvent; internal TMS as reference for ^1H and ^{13}C and external 85% H_3PO_4 as reference for ^{31}P. GCMS: Hewlett−Packard 5890A/Finnigan Incos (70 eV). MS: AEI/Kratos MS50, EI at 70 eV, CI using isobutane.

Addition of Acyl Ylides to Vinyl Ketones: The appropriate vinyl ketone (20.0 mmol) was added to a solution of the appropriate acyl ylide (20.0 mmol) in toluene (250 mL) and the mixture was heated under reflux for 48 h. The solvents were evaporated from the solution and the residual oil digested with diethyl ether for 4 h. The resulting solid product was filtered off and recrystallised from ethyl acetate to give the products as follows.

3-(Triphenylphosphoranylidene)heptane-2,6-dione (3a): From (acetylmethylene)triphenylphosphorane and methyl vinyl ketone (6.0 g, 76%) as colourless prisms, m.p. 158 °C. IR (KBr): ṽ = 3040 cm^{-1}, 2980, 2920, 2900, 1700 (CO), 1510 (CO). ^1H NMR: δ = 7.6−7.4 (m, 15 H, Ph), 2.3−2.2 (m, 4 H, CH_2), 2.13 (s, 3 H, 1-H_3), 1.86 (s, 3 H, 7-H_3) ppm. ^{13}C NMR: See Table 6. ^{31}P NMR: δ = +18.1 ppm. MS: m/z = 388 [M^+]. $C_{25}H_{25}O_2P$ (388.5): calcd. C 77.30, H 6.49; found C 76.86, H 6.25.

3-(Triphenylphosphoranylidene)octane-2,6-dione (3b): From (acetylmethylene)triphenylphosphorane and ethyl vinyl ketone (6.8 g, 85%) as colourless crystals, m.p. 148 °C. IR (KBr): ṽ = 3030 cm^{-1}, 2960, 2920, 2900, 1690 (CO), 1510 (CO), 1470, 1420, 1380, 1140, 1090. ^1H NMR: δ = 7.6−7.4 (m, 15 H, Ph), 2.29−2.23 (m, 4 H, CH_2CH_2), 2.13 (q, J = 7 Hz, $C\mathit{H_2}CH_3$), 2.13 (s, COMe), 0.89 (t, J = 7 Hz, $CH_2C\mathit{H_3}$) ppm. ^{13}C NMR: See Table 6. ^{31}P NMR: δ = +17.5. MS: m/z = 402 [M^+], 387, 345, 331. $C_{26}H_{27}O_2P$ (402.5): calcd. C 77.59, H 6.77; found C 77.84, H 6.52.

1-(4-Methoxyphenyl)-4-(triphenylphosphoranylidene)hexane-1,5-dione (3c): From (acetylmethylene)triphenylphosphorane and 4-methoxyacrylophenone (7.5 g, 78%) as yellow crystals, m.p. 162 °C. IR (KBr): ṽ = 3060 cm^{-1}, 2940, 2860, 1660 (CO), 1590, 1510 (CO), 1250. ^1H NMR: δ = 7.64−7.4 (m, 17 H), 6.81 (d, J = 9 Hz, 2 H), 3.81 (s, 3 H, OMe), 2.81−2.77 (m, 2 H, CH_2), 2.49−2.40 (m, 2 H, CH_2), 2.18 (s, 3 H, COMe) ppm. ^{13}C NMR: See Table 6. ^{31}P NMR: δ = +18.0 ppm. MS: m/z = 480 [M^+], 345, 331. $C_{31}H_{29}O_3P$ (480.6): calcd. C 77.48, H 6.09; found C 77.38, H 5.92.

5-(Triphenylphosphoranylidene)octane-2,6-dione (3d): From (propionylmethylene)triphenylphosphorane and methyl vinyl ketone (6.5 g, 81%) as colourless crystals, m.p. 111 °C. IR (KBr): ṽ = 3040 cm^{-1}, 2960, 2940, 2900, 1700 (CO), 1620, 1510 (CO), 1430, 1100. ^1H NMR: δ = 7.6−7.4 (m, 15 H, Ph), 2.39 (q, J = 8 Hz, 2 H, $C\mathit{H_2}CH_3$), 2.29−2.22 (m, 4 H, CH_2CH_2), 1.86 (s, 3 H, COMe), 1.14 (t, J = 8 Hz, 3 H, $CH_2C\mathit{H_3}$) ppm. ^{13}C NMR: See Table 6. ^{31}P NMR: δ = +16.6 ppm. MS: m/z = 402 [M^+], 359, 345. $C_{26}H_{27}O_2P$ (402.5): calcd. C 77.59, H 6.77; found C 77.74, H 6.89.

4-(Triphenylphosphoranylidene)nonane-3,7-dione (3e): From (propionylmethylene)triphenylphosphorane and ethyl vinyl ketone (6.9 g, 83%) as bright yellow crystals, m.p. 130 °C. IR (KBr): ṽ = 3070 cm^{-1}, 2970, 2930, 2890, 1710 (CO), 1600, 1510 (CO), 1480, 1430, 1100. ^1H NMR: δ = 7.6−7.4 (m, 15 H, Ph), 2.40 (q, J = 8 Hz, 2 H, $CH_2COC\mathit{H_2}CH_3$), 2.30−2.22 (m, 4 H, CH_2CH_2), 2.12 (q, J = 7 Hz, 2 H, P=C−$COC\mathit{H_2}CH_3$), 1.15 (t, J = 8 Hz, 3 H, $CH_2COCH_2C\mathit{H_3}$), 0.88 (t, J = 7 Hz, 3 H, P=C−$COCH_2C\mathit{H_3}$) ppm. ^{13}C NMR: See Table 6. ^{31}P NMR: δ = +16.4 ppm. MS: m/z = 416 [M^+], 387, 359, 345. $C_{27}H_{29}O_2P$ (416.5): calcd. C 77.86, H 7.02; found C 77.28, H 7.22.

1-Phenyl-2-(triphenylphosphoranylidene)hexane-1,5-dione (3f): From (benzoylmethylene)triphenylphosphorane and methyl vinyl ketone

Table 6. ^{13}C NMR spectra [δ_C ($J_{P,C}$)] of the ylides **3** and **5**

	R^1	R^2	P=*C*	*C*OR^1	P=C−*C*H$_2$	*C*H$_2$CO	*C*OR^2	*P*-Phenyl				R^1 signals	R^2 signals
								C-1	C-2	C-3	C-4		
3a	Me	Me	61.8 (106)	187.9 (6)	23.0 (14)	47.9	208.2	126.9 (90)	133.0 (9)	128.3 (12)	131.2 (3)	24.3 (11)	29.2
3b	Me	Et	62.0 (107)	188.1 (6)	23.3 (14)	46.7	211.1	127.1 (89)	133.2 (9)	128.4 (12)	131.3	24.5 (11)	35.4, 7.5
3c	Me	Ar[a]	62.4 (107)	188.3 (6)	24.55 (14)	42.8	198.4	127.2 (90)	133.2 (9)	128.4 (12)	131.3	24.59 (11)	163.0, 130.1 (2 C) 129.6, 113.4 (2 C) 55.2
3d	Et	Me	61.2 (107)	191.6 (5)	22.3 (14)	48.4	208.5	127.3 (90)	133.1 (11)	128.3 (12)	131.2 (3)	29.0 (11), 10.7	29.3
3e	Et	Et	61.3 (105)	191.7 (5)	22.4 (15)	47.1	211.0	127.4 (90)	133.1 (9)	128.4 (12)	131.2 (3)	29.1 (11), 10.7	35.4, 7.5
3f	Ph	Me	64.5 (105)	187.0 (5)	22.7 (14)	47.9	202.3	126.8 (90)	133.2 (9)	128.5 (12)	131.5 (3)	142.6 (12), 127.8 127.7 (2 C) 126.9 (2 C)	29.1
3g	Ph	Et	64.7 (104)	187.0 (5)	22.8 (14)	46.5	210.9	126.9 (92)	133.2 (9)	128.5 (12)	131.5 (3)	142.7 (14), 127.9 127.7 (2 C) 127.0 (2 C)	35.2, 7.4
5a	Me	Me	38.3 (128)	170.9 (18)	22.4 (14)	47.8	209.7	127.6 (89)	133.1 (9)	128.2 (12)	131.4	49.5	29.25
			37.4 (120)	170.0 (14)	21.7 (12)	46.5	209.4	127.0 (91)				48.3	29.16
5b	Me	Et	37.8 (121)	170.2	22.7 (14)	46.6	212.5	127.4 (90)	133.4 (9)	128.6 (12)	131.8	49.8	35.4, 7.6
					22.1	45.2		127.3	132.8 (11)	128.4 (12)	131.6	48.5	
5c	Et	Me	37.6 (121)	170.1 (20)	22.6	46.8	210.1	127.5 (90)	133.4 (9)	128.4 (12)	131.6	57.2, 13.9	29.4
5d	Et	Et	37.5 (120)	169.9 (12)	22.6	46.4	212.4	127.5 (87)	133.3 (11)	128.3 (12)	131.5 (3)	57.6, 15.0	35.3, 7.6
					22.0	45.2		127.4				57.0, 13.8	

[a] R^2 = 4-methoxyphenyl.

(8.0 g, 89%) as yellow crystals, m.p. 175 °C. IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 2940, 2880, 1710 (CO), 1580, 1500 (CO), 1440, 1390, 1110, 1100. ^{1}H NMR: δ = 7.70−7.25 (m, 20 H, Ph), 2.41−2.32 (m, 2 H, CH$_2$), 2.15−2.12 (m, 2 H, CH$_2$), 1.67 (s, 3 H, Me) ppm. ^{13}C NMR: See Table 6. ^{31}P NMR: δ = +16.6 ppm. MS: *m/z* = 450 [M$^+$], 407, 393, 381. $C_{30}H_{27}O_2P$ (450.5): calcd. C 79.98, H 6.04; found C 80.16, H 6.23.

1-Phenyl-2-(triphenylphosphoranylidene)heptane-1,5-dione (3g): From (benzoylmethylene)triphenylphosphorane and ethyl vinyl ketone (8.0 g, 89%) as bright yellow crystals, m.p. 141 °C. IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2960, 2920, 2880, 1700 (CO), 1570, 1490 (CO), 1420, 1380, 1100. ^{1}H NMR: δ = 7.7−7.25 (m, 20 H, Ph), 2.41−2.32 (m, 2 H, CH$_2$), 2.14−2.10 (m, 2 H, CH$_2$), 1.95 (q, *J* = 7 Hz, 2 H, C*H$_2$*CH$_3$), 0.77 (t, *J* = 7 Hz, 3 H, CH$_2$C*H$_3$*) ppm. ^{13}C NMR: See Table 6. ^{31}P NMR: δ = +17.4. MS: = *m/z* = 464 [M$^+$], 407, 393, 379. $C_{31}H_{29}O_2P$ (464.6): calcd. C 80.15, H 6.30; found C 79.66, H 6.40.

Addition of Alkoxycarbonyl Ylides to Vinyl Ketones: The appropriate vinyl ketone (20.0 mmol) was added to a solution of the appropriate alkoxycarbonyl ylide (20.0 mmol) in dichloromethane (250 mL) and the mixture was heated under reflux for 36 h. The solvents were evaporated from the solution and the residue recrystallised from ethyl acetate to give the products as follows:

Methyl 5-Oxo-2-(triphenylphosphoranylidene)hexanoate (5a): From (methoxycarbonylmethylene)triphenylphosphorane and methyl vinyl ketone (7.4 g, 91%) as colourless crystals, m.p. 147 °C. IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2920, 2890, 1700, 1630 (CO), 1470, 1430, 1120, 1090. ^{1}H NMR (2 rotamers): δ = 7.64−7.45 (m, 15 H, Ph), 3.58/3.11 (s, 3 H, OMe), 2.52−2.25 (m, 4 H, CH$_2$CH$_2$), 2.00/1.93 (s, 3 H, COMe) ppm. ^{13}C NMR: See Table 6. ^{31}P NMR: δ = +22.6/22.0 ppm. MS: *m/z* = 404 [M$^+$]. $C_{25}H_{25}O_3P$ (404.5): calcd. C 74.24, H 6.23; found C 74.58, H 6.34.

Methyl 5-Oxo-2-(triphenylphosphoranylidene)heptanoate (5b): From (methoxycarbonylmethylene)triphenylphosphorane and ethyl vinyl ketone (7.7 g, 92%) as colourless crystals, m.p. 104 °C. IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 3020, 2980, 2940, 2910, 1700, 1620 (CO), 1440, 1310, 1100. ^{1}H NMR (2 rotamers): δ = 7.63−7.45 (m, 15 H, Ph), 3.58/3.11 (br. s, 3 H, OMe), 2.51−2.25 (m, 4 H, CH$_2$CH$_2$), 2.33 (q, *J* = 7 Hz, 2 H, C*H$_2$*CH$_3$), 0.92 (t, *J* = 7 Hz, 3 H, CH$_2$C*H$_3$*) ppm. ^{13}C NMR: See Table 6. ^{31}P NMR: δ = +23.3/22.8 ppm. MS: *m/z* = 418 [M$^+$], 387, 347. $C_{26}H_{27}O_3P$ (418.5): calcd. C 74.62, H 6.51; found C 74.90, H 6.51.

Ethyl 5-Oxo-2-(triphenylphosphoranylidene)hexanoate (5c): From (ethoxycarbonylmethylene)triphenylphosphorane and methyl vinyl ketone (7.3 g, 87%) as colourless crystals, m.p. 106 °C. IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3020, 2980, 2900, 1700, 1600 (CO), 1440, 1310, 1290, 1100. ^{1}H NMR (2 rotamers): δ = 7.64−7.44 (m, 15 H, Ph), 4.03/3.70 (br. s, 2 H, C*H$_2$*CH$_3$), 2.49 (m, 2 H, CH$_2$), 2.28−2.20 (m, 2 H, CH$_2$), 2.00 (s, 3 H, COMe), 1.25/0.44 (br. s, 3 H, CH$_2$C*H$_3$*) ppm. ^{13}C NMR: See Table 6. ^{31}P NMR: δ = +22.5 ppm. MS: *m/z* = 418 [M$^+$], 373, 361. $C_{26}H_{27}O_3P$ (418.5): calcd. C 74.62, H 6.51; found C 74.97, H 6.71.

Ethyl 5-Oxo-2-(triphenylphosphoranylidene)heptanoate (5d): From (ethoxycarbonylmethylene)triphenylphosphorane and ethyl vinyl ketone (7.4 g, 86%) as colourless crystals, m.p. 117 °C. IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3020, 2980, 2920, 1700, 1610 (CO), 1440, 1310, 1290, 1100, 1090. ^{1}H NMR (2 rotamers): δ = 7.64−7.46 (m, 15 H, Ph), 4.05/3.70 (br. s, 2 H, OC*H$_2$*CH$_3$), 2.50−2.22 (m, 6 H, CH$_2$CH$_2$, COC*H$_2$*CH$_3$), 0.93 (t, *J* = 7 Hz, 3 H, COCH$_2$C*H$_3$*), 1.20/0.44 (br. s, 3 H, OCH$_2$C*H$_3$*) ppm. ^{13}C NMR: See Table 6. ^{31}P NMR: δ = +23.6/22.5 ppm. MS: *m/z* = 432 [M$^+$], 387, 361. $C_{27}H_{29}O_3P$ (432.5): calcd. C 74.98, H 6.76; found C 75.11, H 6.52.

Flash Vacuum Pyrolysis of Ylides 3 and 5: The apparatus used was as described previously.[22] All pyrolyses were conducted at pressures in the range 10^{-2} to 10^{-1} Torr and were complete within 2 h. Under these conditions the contact time in the hot zone was estimated to be about 10 ms. In all cases Ph_3PO collected at the furnace exit and the more volatile products were recovered from the cold trap. Yields were determined either by isolation or, for small-scale experiments, by calibration of the ^{1}H NMR spectra by adding an accurately weighed quantity of a solvent such as CH_2Cl_2 and comparing integrals, a procedure estimated to be accurate to within ±10%.

FVP of 3-(Triphenylphosphoranylidene)heptane-2,6-dione (3a): FVP of the title ylide **3a** (5.0 g) at 650 °C gave a solid at the furnace exit which was shown to be Ph_3PO by ^{31}P NMR spectroscopy. The liquid in the cold trap consisted of three compounds. **Methyl Vinyl Ketone (2a):** 32%. ^{1}H NMR: $\delta = 6.32$ (half AB pattern of d, J = 18, 10 Hz, 1 H), 6.21 (half AB pattern of d, J = 18, 2 Hz, 1 H), 5.92 (dd J = 10, 2 Hz, 1 H), 2.29 (s, 3 H). ^{13}C NMR: $\delta = 199.1$, 137.4, 129.1, 26.4 ppm. **Propyne (15a):** ^{1}H NMR: $\delta = 1.82$ (s, 4 H) ppm. ^{13}C NMR: $\delta = 80.0$ (≡C−), 67.4 (≡CH), 3.2 ppm. **Hept-5-yn-2-one (14a):** Kugelrohr distillation gave **14a** (0.37 g, 26%) as a colourless oil. IR: $\tilde{\nu} = 1718\ cm^{-1}$. ^{1}H NMR: $\delta = 2.63$ (t, J = 7 Hz, 2 H), 2.38 (t of q, J = 7, 2 Hz, 2 H), 2.17 (s, 3 H), 1.75 (t, J = 2 Hz, 3 H) ppm. ^{13}C NMR: $\delta = 207.4$ (CO), 77.7 (≡C−), 76.2 (≡C−), 42.9 ($COCH_2$), 29.9 (CO*Me*), 13.4 ($\equiv C-CH_2$), 3.4 (≡C−*Me*) ppm. MS (CI): m/z = (%) = 111 (100) $[M + H^+]$, 97 (10), 85 (6). $C_7H_{11}O$ $[M + H^+]$: calcd. 111.0810; found 111.0814 (MS). The pyrolysis was repeated as above but at 500 °C (99.5 mg) and gave **14a** (10%), **2a** (14%) and **15a** while at 750 °C (43.1 mg) the products were **14a** (33%), **2a** (28%) and **15a**.

FVP of 3-(Triphenylphosphoranylidene)octane-2,6-dione (3b): FVP of the title ylide **3b** (36.9 mg) at 650 °C gave a solid at the furnace exit which was shown to be Ph_3PO by ^{31}P NMR spectroscopy. The liquid in the cold trap consisted of three products. **Oct-6-yn-3-one (14b):** 39%. ^{1}H NMR: $\delta = 2.47$ (q, J = 7 Hz, 2 H, CH_2CH_3), 2.6−2.35 (m, 4 H, CH_2CH_2), 1.74 (t, J = 2 Hz, 3 H, COMe), 1.07 (t, J = 7 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR: $\delta = 209.9$ (CO), 77.8 (≡C−), 76.0 (≡C−), 41.5 ($COCH_2CH_2$), 36.0 $COCH_2CH_3$), 13.4 ($\equiv C-CH_2$), 7.7 (CH_2Me), 3.4 (≡C−*Me*) ppm. **Ethyl Vinyl Ketone (4b):** 49%. ^{1}H NMR: $\delta = 6.44$ (half AB pattern of d, J = 18, 10 Hz, 1 H), 6.23 (half AB pattern of d, J = 18, 2 Hz, 1 H), 5.85 (dd, J = 10, 2 Hz, 1 H), 2.63 (q, J = 7 Hz, 2 H), 1.13 (t, J = 7 Hz, 3 H) ppm. ^{13}C NMR: $\delta = 202.0$, 136.4, 127.8, 32.8, 7.9 ppm. **Propyne:** ^{1}H and ^{13}C NMR as in FVP of **3a**.

FVP of 1-(4-Methoxyphenyl)-4-(triphenylphosphoranylidene)hexane-1,5-dione (3c): FVP of the title ylide **3c** (77 mg) at 650 °C gave a solid at the furnace exit which was shown to be Ph_3PO by ^{31}P NMR spectroscopy. The liquid in the cold trap contained two products. **4-Methoxyacrylophenone (2c):** 79%. ^{1}H NMR: $\delta = 7.97$ (d, J = 5 Hz, 2 H), 7.19 (dd, J = 18, 10 Hz, 1 H), 6.97 (d J = 5 Hz, 2 H), 6.44 (dd, J = 18, 2 Hz, 1 H), 5.85 (dd, J = 10, 2 Hz, 1 H), 3.87 (s, 3 H) ppm. ^{13}C NMR: $\delta = 189.3$ (CO), 163.6 (Ar-C-4), 132.2 (=CH_2), 131.1 (2 C, Ar-C-2, C-6), 129.3 (COCH=), 126.5 (Ar-C-1), 113.9 (2 C, Ar-C-3, C-5), 55.5 (OMe) ppm. **Propyne:** ^{1}H and ^{13}C NMR as in FVP of **3a**.

FVP of 4-(Triphenylphosphoranylidene)octane-3,7-dione (3d): FVP of the title ylide **3d** (15.2 mg) at 650 °C gave a solid at the furnace exit which was shown to be Ph_3PO by ^{31}P NMR spectroscopy. The liquid in the cold trap appeared to consist of three products. **5-Methyl-4-methylenehexa-1,5-dien-3-one (18):** ^{1}H NMR: δ = 6.95−6.80 (m, 2 H), 6.65−6.55 (m, 1 H), 5.94, 5.65, 5.28, 5.14 (4 × s, 4 × 1 H), 1.93 (m, 3 H) ppm. ^{13}C NMR: $\delta = 196.4$, 142.6, 137.5 (2 C), 129.1, 122.8, 117.0, 20.8 ppm. **Methyl Vinyl Ketone:** ^{1}H and ^{13}C NMR as in FVP of **3a**. **But-1-yne (15d):** Possibly.

FVP of 1-Phenyl-2-(triphenylphosphoranylidene)hexane-1,5-dione (3f): FVP of the ylide **3f** (56 mg) at 650 °C gave a solid at the furnace exit which was shown to be Ph_3PO by ^{31}P NMR spectroscopy. The liquid in the cold trap consisted of three products. **6-Phenylhex-5-yn-2-one (14f):** 16%. IR: $\tilde{\nu} = 1721\ cm^{-1}$. ^{1}H NMR: δ = 7.55−7.25 (m, 5 H), 2.80−2.65 (m, 4 H), 2.21 (s, 3 H). ^{13}C NMR: $\delta = 191.5$ (CO), 131.6 (Ph C-2, C-6), 128.3 (Ph C-3, C-5), 128.2 (Ph C-4), 84.0 (≡C−), 77.2 (≡C−), 42.5 ($COCH_2$), 30.0 (CO*Me*), 14.0 ($\equiv C-CH_2$) [signal for Ph C-1 not apparent] ppm. **Methyl Vinyl Ketone:** 29%. ^{1}H and ^{13}C NMR as in FVP of **3a**. **Ethynylbenzene (15f):** 10%. ^{1}H NMR: δ = 7.55−7.31 (m, 5 H), 3.09 (s, 1 H) ppm. ^{13}C NMR: $\delta = 132.1$ (C-2, C-6), 128.8 (C-4), 128.3 (C-3, C-5), 122.3 (C-1), 83.6 (≡C−), 77.1 (≡CH) ppm.

FVP of 1-Phenyl-2-(triphenylphosphoranylidene)heptane-1,5-dione (3g): FVP of the title ylide **3g** (16.2 mg) at 650 °C gave a solid at the furnace exit which was shown to be Ph_3PO by ^{31}P NMR spectroscopy. The liquid in the cold trap contained three products. **Ethyl Vinyl Ketone:** 36%. ^{1}H and ^{13}C NMR as in FVP of **3b**. **Ethynylbenzene:** 42%. ^{1}H and ^{13}C NMR as in FVP of **3f**. **7-Phenylhept-6-yn-3-one (14g):** 20%. ^{1}H NMR: δ = 7.60−7.25 (m, 5 H), 2.75−2.45 (m, 6 H), 1.09 (t, J = 7 Hz, 3 H) ppm.

FVP of Methyl 5-Oxo-2-(triphenylphosphoranylidene)hexanoate (5a): FVP of the title ylide **5a** (56.4 mg) at 650 °C gave a solid at the furnace exit which was shown to be Ph_3PO by ^{31}P NMR spectroscopy. The liquid in the cold trap contained one product. **Methyl 3-Methyl-2-methylenebut-3-enoate (20a):** 47% as a yellow liquid. ^{1}H NMR: δ = 5.93, 5.64, 5.27, 5.12 (4 × s, 4 × 1 H, = CH_2), 3.80 (s, 3 H, OMe), 1.95 (s, 3 H, C−Me) ppm. ^{13}C NMR: See Table 7. $C_7H_{10}O_2$: calcd. 126.0681; found 126.0684 (MS). Reaction of **5a** on a larger scale (1.07 g) at 700 °C gave **20a** (0.20 g, 60%) as a yellow liquid. Attempted kugelrohr distillation of **20a** from a repeat preparation caused dimerisation to yield a 1:1 mixture: **Dimethyl 4-Methyl-1-isopropenylcyclohex-3-ene-1,3-dicarboxylate (21a) and Dimethyl 3-Methyl-1-isopropenylcyclohex-3-ene-1,4-dicarboxylate (22a):** 14% as a colourless liquid, b.p. 160−170 °C/20 Torr. IR: $\tilde{\nu} = 1690\ cm^{-1}$, 1630, 1060, 890. ^{1}H NMR: δ = 4.98 (s, 1 H), 4.85 (s, 1 H), 3.72 (s, 3 H), 3.69 (s, 3 H), 2.8−2.2 (m, 6 H), 2.10 (s, 3 H), 1.75 (s, 3 H) ppm. ^{13}C NMR: $\delta = 175.0$, 169.6, 145.1, 144.8, 122.8, 112.1 (=CH_2), 52.2, 51.2, 50.6, 47.0, 40.8, 34.6, 27.9, 26.1, 24.7, 24.1, 21.7, 19.7 ppm. MS: m/z (%) = 252 (11) $[M^+]$, 220 (65), 193 (50), 161 (100), 133 (86), 121 (82), 93 (80). $C_{14}H_{20}O_4$: calcd. 252.1362; found 252.1370 (MS).

Table 7. ^{13}C NMR spectra of dienes **20**

Compound	CO	=C<	=CH_2	R^1 signals	R^2 signals
20a	167.8	142.6, 139.8	122.8, 117.0	52.0	21.4
20b	167.6	146.9, 142.5	124.0, 114.3	52.0	27.5, 12.5
20c	167.3	142.9, 139.8	122.4, 116.9	60.9, 14.2	21.4
20d	167.2	147.0, 142.9	123.5, 114.2	60.9, 14.2	27.4, 12.6

FVP of Methyl 5-Oxo-2-(triphenylphosphoranylidene)heptanoate (5b): FVP of the title ylide **5b** (800 mg) at 650 °C gave a solid at the furnace exit which was shown to be Ph_3PO by ^{31}P NMR spectroscopy. The liquid in the cold trap proved to be: **Methyl 2,3-Dimethylenepentanoate (20b):** 160 mg, 60% as a colourless liquid. ^{1}H NMR: δ = 6.02, 5.65, 5.16, 5.09 (4 × s, 4 × 1 H, =CH_2), 3.79

(s, 3 H), 2.30 (q, J = 8 Hz, 2 H), 1.05 (t, J = 8 Hz, 3 H) ppm. ^{13}C NMR: See Table 7. $C_8H_{12}O_2$: calcd. 140.0837; found 140.0840 (MS). Attempted kugelrohr distillation of **20b** caused dimerisation to yield a 1:1 mixture: **Dimethyl 1-(But-1-en-2-yl)-3-ethylcyclohex-3-ene-1,4-dicarboxylate (21b) and Dimethyl 1-(But-1-en-2-yl)-4-ethylcyclohex-3-ene-1,3-dicarboxylate (22b):** 12% as a colourless liquid, b.p. 100 °C/0.1 Torr. MS: m/z = (%) = 280 (14) [M$^+$], 248 (82), 221 (40), 192 (65), 189 (85), 135 (100). $C_{16}H_{24}O_4$ calcd. 280.1675; found 280.1678 (MS).

FVP of Ethyl 5-Oxo-2-(triphenylphosphoranylidene)hexanoate (5c): FVP of the title ylide **5c** (29.6 mg) at 650 °C gave a solid at the furnace exit which was shown to be Ph_3PO by ^{31}P NMR spectroscopy. The liquid in the cold trap was: **Ethyl 3-Methyl-2-methylenebut-3-enoate (20c):** 40%. ^{1}H NMR: δ = 5.93, 5.62, 5.30, 5.12 (4 × s, 4 × 1 H, =CH_2), 4.25 (q, J = 8 Hz, 2 H), 1.95 (s, 3 H), 1.32 (t, J = 8 Hz, 3 H). ^{13}C NMR: see Table 7. $C_8H_{12}O_2$: calcd. 140.0837; found 140.0843 (MS). Reaction of **5c** on a larger scale (1.39 g) at 500 °C gave **20c** (0.11 g, 24%) as a colourless liquid while using **5c** (1.60 g) at 700 °C gave **20c** (0.27 g, 50%). Attempted kugelrohr distillation of **20c** caused dimerisation to yield a 1:1 mixture: **Diethyl 3-Methyl-1-(propen-2-yl)cyclohex-3-ene-1,4-dicarboxylate (21c) and Diethyl 4-Methyl-1-(propen-2-yl)cyclohex-3-ene-1,3-dicarboxylate (22c):** MS: m/z (%) = 280 (11) [M$^+$], 234 (60), 207 (42), 161 (100), 133 (60), 121 (56), 93 (65). $C_{16}H_{24}O_4$: calcd. 280.1675; found 280.1668 (MS).

FVP of Ethyl 5-Oxo-2-(triphenylphosphoranylidene)heptanoate (5d): FVP of the title ylide **5d** (14.1 mg) at 650 °C gave a solid at the furnace exit which was shown to be Ph_3PO by ^{31}P NMR spectroscopy. The liquid in the cold trap was: **Ethyl 2,3-Dimethylenepentanoate (20d):** 41%. ^{1}H NMR: δ = 6.00, 5.63, 5.16, 5.08 (4 × s, 4 × 1 H, =CH_2), 4.25 (q, J = 8 Hz, 2 H, OCH_2CH_3), 2.30 (q, J = 8 Hz, 2 H, C-CH_2CH_3), 1.31 (t, J = 8 Hz, 3 H, OCH_2CH_3), 1.06 (t, J = 8 Hz, 3 H, C-CH_2CH_3) ppm. ^{13}C NMR: see Table 7. $C_9H_{14}O_2$: calcd. 154.0994; found 154.0989 (MS). Reaction of **5d** on a larger scale (1.03 g) at 500 °C gave **20d** (0.062 g, 17%) as a colourless liquid while using **5d** (1.19 g) at 700 °C gave **20d** (0.19 g, 44%). Attempted kugelrohr distillation of **20d** caused dimerisation to yield a 1:1 mixture: **Diethyl 1-(But-1-en-2-yl)-3-ethylcyclohex-3-ene-1,4-dicarboxylate (21d) and Diethyl 1-(But-1-en-2-yl)-4-ethylcyclohex-3-ene-1,3-dicarboxylate (22d):** MS: m/z (%) = 308 (10) [M$^+$], 262 (65), 235 (28), 192 (60), 189 (80), 154 (48), 135 (100). $C_{18}H_{28}O_4$: calcd. 308.1988; found 308.1994 (MS).

Diels−Alder Reaction of Dienes 20 with Maleic Anhydride: FVP of the appropriate ylide **5** (1.0 g, ca. 2.4 mmol) was completed as usual at 650 °C. The liquid in the cold trap was quickly dissolved in dry toluene (2 mL) and a solution of maleic anhydride (0.24 g, 2.4 mmol) in toluene (8 mL) was added. The solution was heated under reflux for 2 h and then concentrated to yield a pale brown liquid, which crystallised. Recrystallisation from ethyl acetate and a small amount of diethyl ether gave the products as follows.

***cis*-1-Methoxycarbonyl-2-methylcyclohexene-4,5-dicarboxylic Anhydride 23a from Ylide 5a:** 177 mg, 32% as colourless crystals, m.p. 129−132 °C. ^{1}H NMR (CD_3COCD_3): δ = 3.70 (s, 3 H), 3.08 (m, 2 H), 2.95−2.50 (m, 4 H), 2.05 (s, 3 H). ^{13}C NMR: (CD_3COCD_3): δ = 174.3 (2 × anhydride CO), 166.9 (ester CO), 145.6 (C=C), 123.1 (C=C), 51.4 (OMe), 39.81, 39.78, 34.8, 28.1, 21.7 (Me). MS: m/z (%) = 224 (6) [M$^+$], 210 (100), 192 (85), 165 (50), 151 (46), 119 (30), 93 (75), 91 (60). $C_{11}H_{12}O_5$: calcd. 224.0685; found 224.0679 (MS).

***cis*-2-Ethyl-1-methoxycarbonylcyclohexene-4,5-dicarboxylic Anhydride 23b from Ylide 5b:** 228 mg, 40% as colourless crystals, m.p. 134−137 °C. ^{1}H NMR (CD_3COCD_3): δ = 3.70 (s, 3 H), 3.15−3.02 (m, 2 H), 2.90−2.50 (m, 4 H), 2.45−2.30 (q, J = 7 Hz, 2 H), 1.05 (t, J = 7 Hz, 3 H) ppm. ^{13}C NMR: (CD_3COCD_3): δ = 174.5, 174.4 (2 × anhydride C=O), 167.0 (ester CO), 150.7 (C=C), 122.8 (C=C), 51.4 (OMe), 39.8 (2 C), 32.3, 28.6, 28.0 (CH_2Me), 13.1 (CH_2Me) ppm. MS: m/z (%) = 238 (2) [M$^+$], 225 (26), 224 (100), 206 (84), 179 (35), 133 (35), 107 (50), 105 (50). $C_{12}H_{14}O_5$ (238.3): calcd. C 60.50, H 5.93; found C 60.76, H 5.91.

***cis*-1-Ethoxycarbonyl-2-methylcyclohexene-4,5-dicarboxylic Anhydride 23c from Ylide 5c:** 216 mg, 38% as colourless crystals, m.p. 133−135 °C. ^{1}H NMR (CD_3COCD_3): δ = 4.20−4.10 (q, J = 7 Hz, 2 H), 3.15−3.05 (m, 2 H), 2.90−2.50 (m, 4 H), 2.07 (s, 3 H), 1.28 (t, J = 7 Hz, 3 H) ppm. ^{13}C NMR: (CD_3COCD_3): δ = 174.6, 174.4 (2 × anhydride C=O), 167.0 (ester CO), 145.2 (C=C), 123.5 (C=C), 60.5 (OCH_2Me), 39.9, 39.8, 34.8, 28.1, 21.7 (=CMe), 14.6 (OCH_2Me) ppm. MS: m/z (%) = 238 (57) [M$^+$], 165 (94), 99 (55), 93 (100). $C_{12}H_{14}O_5$: calcd. 238.0841; found 238.0850 (MS).

***cis*-1-Ethoxycarbonyl-2-ethylcyclohexene-4,5-dicarboxylic Anhydride 23d from Ylide 5d:** 175 mg, 30% as colourless crystals, m.p. 148−150 °C. ^{1}H NMR (CD_3COCD_3): δ = 4.15 (q, J = 7 Hz, 2 H), 3.05 (m, 2 H), 2.8−2.3 (m, 6 H), 1.26 (t, J = 7 Hz, 3 H), 1.00 (t, J = 7 Hz, 3 H) ppm. ^{13}C NMR (CD_3COCD_3): δ = 174.7, 174.5 (2 × anhydride CO), 166.7 (ester CO), 150.1 (C=C), 123.1 (C=C), 60.6 (OCH_2), 39.9 (2 C), 32.4, 28.7, 28.0 (CH_2Me), 14.7 (OCH_2Me), 13.3 (CH_2Me) ppm. MS: m/z (%) = 252 (2) [M$^+$], 206 (100), 179 (20), 151 (22), 133 (35), 105 (42). $C_{13}H_{16}O_5$ (252.3): calcd. C 61.89, H 6.40; found C 61.65, H 6.36.

Kinetic Studies

Reaction Setup: Preliminary kinetic results were obtained with a system featuring a Eurotherm 093 pyrolysis unit coupled to a Perkin−Elmer Sigma 115 Gas Chromatograph. The kinetic data reported are from a reactor setup including an HPLC (BioRad Model 2700) fitted with a UV/Vis detector (BioRad Model 1740) adjusted to 254 nm; HPLC column LC-8, 25 cm, 4.6μm (Supelco); and CDS custom-made pyrolysis unit for the thermolysis reactions. The pyrolysis tube is jacketed by an insulating aluminum block fitted with a platinum resistance thermometer and a thermocouple connected to a Comark microprocessor thermometer.

Kinetic Runs and Data Analysis: Aliquots (0.2 mL) of very dilute solutions (ppm) of neat substrates in acetonitrile as solvent and chlorobenzene as internal standard were pipetted into the reaction tube, which was then sealed under vacuum (0.2 Torr). The tube was then placed inside the pyrolyzer for 600 s at a temperature at which 10−20% pyrolysis is deemed to occur. The contents of the tube were analyzed using HPLC. At least three kinetic runs were carried out for each 5−10 °C rise in temperature of the pyrolyzer and for the same time interval until 90−95% pyrolysis was achieved. The reactions were ascertained to be homogeneous, unimolecular, and free of reactor surface effects. The homogeneous nature of the reactions was tested by comparing rates using a normal reactor with those obtained when the reactor vessel was packed with helices. The absence of free radical pathways in the elimination reactions was confirmed using established procedures. The rates were monitored over a temperature range of 20 to 40 K, and the rate coefficients were calculated using the expression for a first-order reaction, $kt = \ln(a_o/a)$ (Table 8). Each rate coefficient represents the mean of three kinetic runs in agreement to within ±2%. The Arrhenius parameters were obtained from a plot of log k against $1/T$ [K]. The Arrhenius plots are linear up to about 95% reaction. Rate constants adjusted to 400 K are given in Table 5.

Table 8. Kinetic data for the gas-phase elimination reaction of selected ylides **3** and **5**

	R^1	R^2	10^4k [s^{-1}] T [K]					$\log_{10}A$ [s^{-1}]	E_a [kJ·mol^{-1}]
3a	Me	Me	1.04	3.04	5.38	10.78	30.21	10.79 ± 0.51	115.34 ± 4.21
			409.05	419.65	428.15	438.35	453.15		
3b	Me	Et	3.94	6.04	9.24	14.90		8.46 ± 0.39	100.59 ± 3.35
			442.25	450.05	457.25	464.85			
3f	Ph	Me	2.16	5.51	12.27	36.74		13.79 ± 0.88	160.94 ± 8.39
			481.10	492.95	504.90	516.90			
3g	Ph	Et	1.21	2.07	6.30	11.90	20.90	12.30 ± 0.94	146.19 ± 8.79
			470.35	479.95	490.50	501.05	510.75		
5a	Me	Me	1.69	3.70	8.91	14.84	24.54	12.63 ± 0.68	143.64 ± 6.22
			458.05	467.05	476.80	484.85	493.40		
5b	Me	Et	1.36	4.12	8.13	14.20	24.59	11.86 ± 1.04	138.52 ± 9.66
			461.95	472.35	482.20	491.75	501.40		
5c	Et	Me	3.35	4.75	8.14	11.95	21.52	10.10 ± 0.02	118.74 ± 1.66
			456.75	461.90	470.15	476.10	485.65		
5d	Et	Et	1.76	2.57	4.51	12.52	26.56	10.96 ± 1.06	128.59 ± 9.66
			454.20	462.90	472.35	483.75	494.95		

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