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New reactions and reactive intermediates in the pyrolysis of cyclic phosphonium ylides

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Dedicated to Professor Oleg A. Rakitin on the occasion of his 65th birthday

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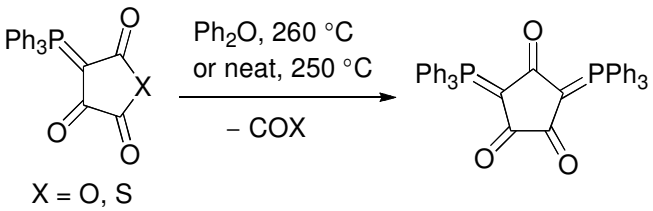
Abstract

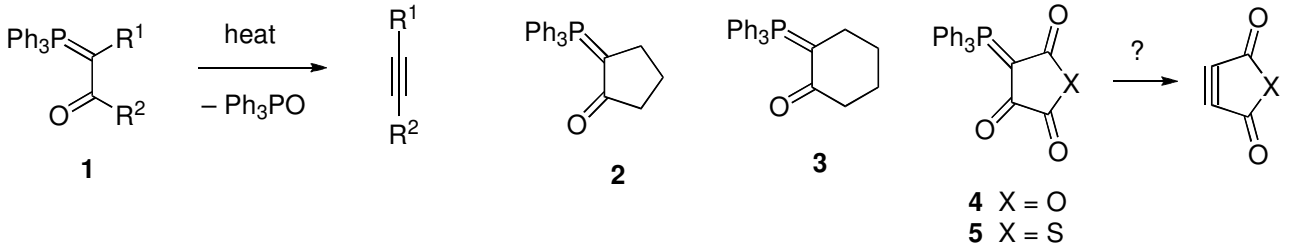
Pyrolysis, either neat or in diphenyl ether solution, results in the conversion of both 4-triphenylphosphoranylidenetetrahydrofuran-2,3,5-trione and 4-triphenylphosphoranylidenetetrahydrothio--phene-2,3,5-trione into 3,5-bis(triphenylphosphoranylidene)cyclopentane-1,2,4-trione. These reactions involve extrusion of CO_2 or COS to give 3-triphenylphosphoranylidenecyclopropane-1,2-dione which further loses CO to give triphenylphosphoranylideneketene. The precise way in which these two reactive phosphorus compounds combine to give the observed product has been examined by chemical and isotopic labelling studies. Cyclotrimerization of triphenylphosphoranylideneketene upon thermolysis in diphenyl ether has also been observed for the first time. The erroneous literature interpretation of the ^{13}C NMR spectrum for triphenylphosphoranylideneketene is corrected.



Keywords: Cyclic ylides, pyrolysis, phosphoranes, reactive intermediates

Introduction

We recently introduced the value of the two-bond NMR coupling constant $^2J_{P–CO}$ as a diagnostic parameter for the reactivity of β-oxophosphonium ylides **1** towards thermal extrusion of Ph_3PO to give alkynes (Scheme 1).[1] All known ylides that do undergo such extrusion to form an alkyne have $^2J_{P–CO}$ < 11 Hz, while those with values above this do not. The latter group includes formyl and alkoxycarbonyl ylides (R^2 = H, O-Alkyl) where the failure of extrusion as well as the high *J* value is associated with the C=P and C=O functions being aligned *anti* rather than *syn* to one another. However the rule also applies to ylides where the functions are constrained *syn* such as the cyclic examples **2** and **3**. With a *J* value of 11.3 Hz, **2** does not undergo extrusion under any circumstances whereas **3** with a value of 3.7 Hz readily eliminates Ph_3PO upon flash vacuum pyrolysis (FVP) at 750 °C to give products derived from cyclohexyne.[1]



1 **2** **3**

4 X = O
5 X = S

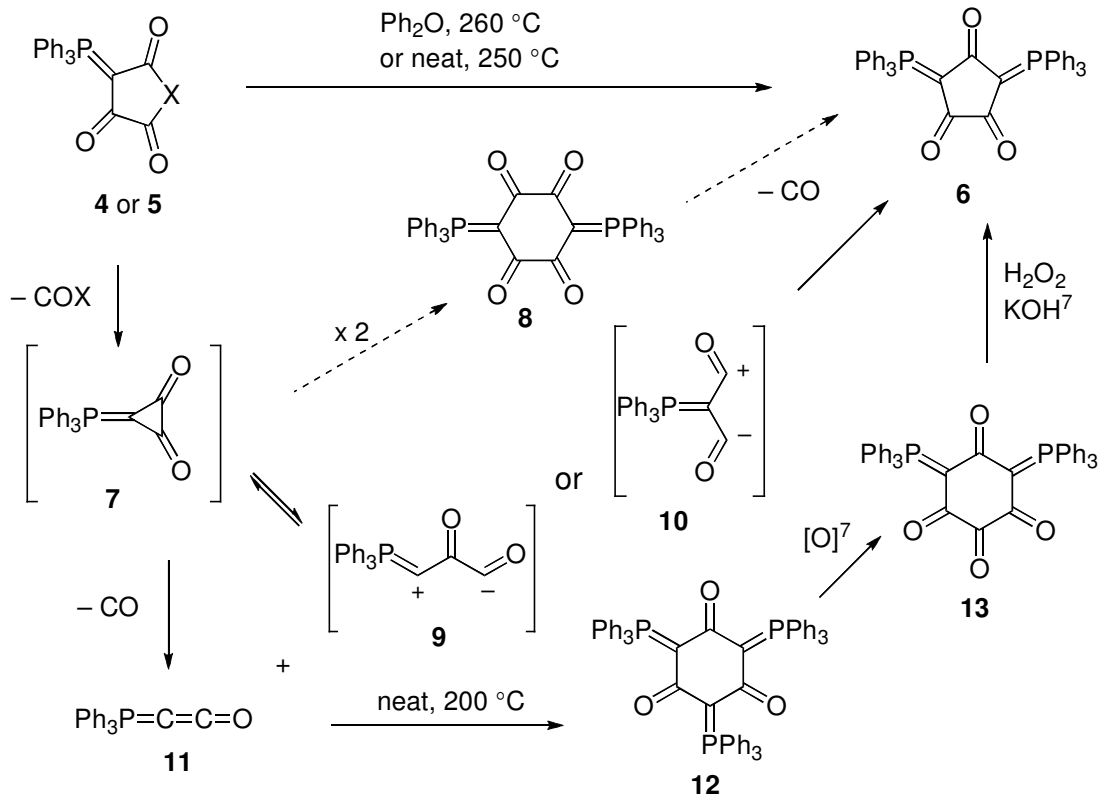
Scheme 1

A wide range of heterocyclic phosphonium ylides are known,[2,3] and among those with published $^2J_{P–CO}$ values, our attention was drawn to ylide **4** and its thio-analogue **5**. These are readily prepared from dichloromaleic (thio)anhydride and, with $^2J_{P–CO}$ values for the ketone carbonyl of 8 Hz[4] and 7 Hz[5] respectively, seemed possible precursors for thermal generation of dehydromaleic anhydride and its thio analogue. Such heterocyclic alkynes are elusive and highly reactive compounds that have attracted considerable interest,[6] and we describe here for the first time the thermal decomposition of **4** and **5**.

Results and Discussion

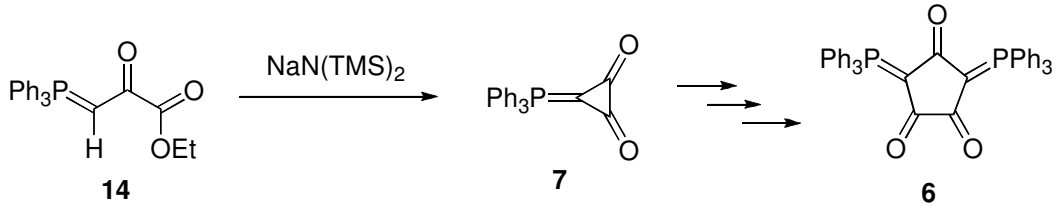
In fact, FVP of both **4** and **5** gave disappointing results, with the only products obtained in the cold trap being a trace of Ph_3PO in the first case and a mixture of Ph_3PO, Ph_3PS, Ph_3P and triphenylphosphoranylideneketene **11** in the second. However there was also substantial decomposition in the inlet tube and analysis of the residue from attempted FVP of **4** at 200 ˚C showed it, most surprisingly, to be the trioxo bis(ylide) **6** (10%) previously reported by Bestmann and co-workers.[7] This must obviously be formed by an intermolecular process and, once this was clear, much better results could be obtained by heating **4** or **5** in a small volume of boiling diphenyl ether (bp 260 ˚C) for 24 h or in the case of **4** by heating the neat material at 250 ˚C for 3 h. In each case the major product was the trioxo bis(ylide) **6** which was readily identified by its characteristic NMR spectra [δ_P +9.0; δ_C 196.4 (t, *J* 10) and 187.6 (dd, *J* 20, 6)] and also by comparison with an authentic sample.

There are several mechanistic possibilities for the formation of this unexpected product (Scheme 2). It seems likely that either CO_2 or COS is first lost to give the triphenylphosphoranylidenecyclopropanedione **7** which may then dimerise probably by way of the dipolar ring-opened forms **9** or **10** to give **8** and this could then lose CO to give **6**. Of course the diradical intermediates corresponding to **9** or **10** could also be considered but these seem less likely in view of the highly polar groups present. A second major possible route is for **7** to



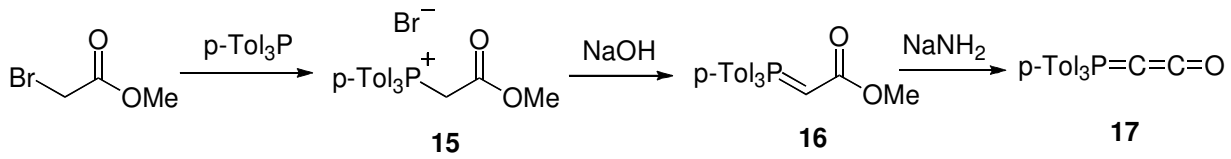
Scheme 2

lose CO to give **11** which can then undergo direct cycloaddition with **9** or **10** to give **6**. Evidence in favour of the latter pathway was provided by heating an equimolar mixture of **4** and **11**[8,9] in boiling diphenyl ether for 2 h, which led to formation of **6** as the only phosphorus-containing product. Interestingly a control experiment of heating **11** alone for 30 min under these conditions led to formation of its cyclic trimer **12** (δ_P +13.9) which was previously obtained by Bestmann and co-workers by a different route.[7] We can thus conclude that whatever intermediate (**9** or **10**) is being formed by **4** in its decomposition to **6** reacts efficiently with added **11** to give the same product. Compound **6** was previously prepared by HCl catalysed trimerisation of **11** to give **12** which was then subjected to oxidation by 2-tosyl-3-phenyloxaziridine to afford the tetraoxo bis(ylide) **13**. This underwent oxidative ring-contraction upon treatment with hydrogen peroxide and KOH to afford **6**. However an additional lower-yielding route to **6** is the treatment of ethyl triphenylphosphoranylidenepyruvate **14** with sodium hexamethyldisilazide to give the product in 4% isolated yield (Scheme 3).[10] This was carried out in the expectation of isolating **7** and, although the author proposed that **6** was formed by a different route not involving **7**, the new evidence presented here makes it likely that this route may also proceed by initial base-induced elimination of ethanol from **14** to give **7** which thereafter reacts as shown in Scheme 2 to give **6**.



Scheme 3

In order to differentiate between the possible modes of bond breaking in **7**, we first attempted chemical labelling by preparing a tri-*p*-tolyl analogue. We were unable to obtain the tri-*p*-tolyl analogue of **4** but the tri-*p*-tolyl analogue of **11**, compound **17**, was prepared as shown in Scheme 4. Ethyl bromoacetate was reacted with tri-*p*-tolylphosphine[11] to give the salt **15** and treatment of this with sodium hydroxide gave the new stabilised ylide **16**, which was fully characterised.

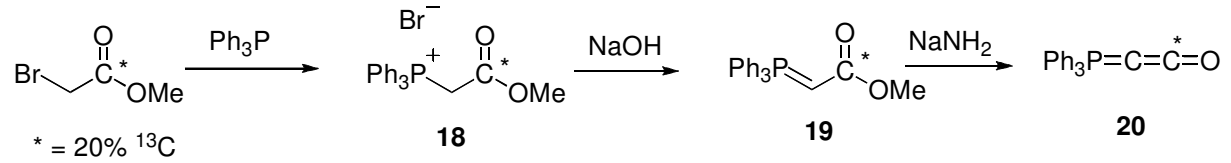


15 **16** **17**

Scheme 4

When this was reacted with sodium amide in toluene a new product with characteristic NMR signals at δ_P +5.3 and δ_C 142.6 (d, *J* 39, P=C=C=O) attributed to **17** was formed. However heating this under a wide variety of conditions, either with or without added **4**, did not lead to formation of a *p*-tolyl analogue of **6** and tri-*p*-tolylphosphine oxide was the only identifiable product derived from **17**.

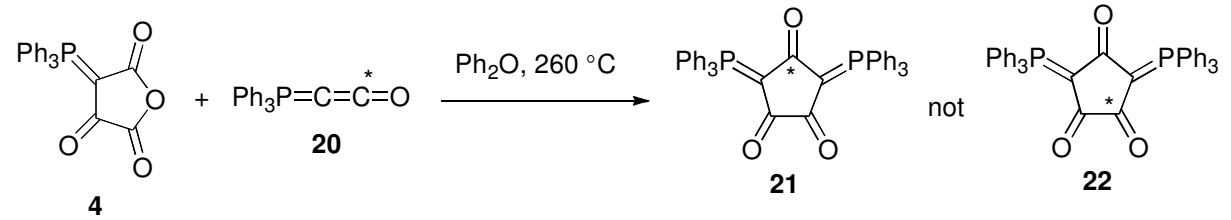
We then resorted to isotopic labelling and prepared 20% ^{13}C-labelled methoxycarbonyl ylide **19** by the literature method[12] starting from labelled methyl bromoacetate via the phosphonium salt **18** (Scheme 5).



18 **19** **20**

Scheme 5

When this was heated in diphenyl ether with **4** the resulting sample of the trioxo bis(ylide) proved to be the isomer **21** with the label at the isolated carbonyl (*ca*. 20 x enhancement of signal at δ_C 196.4 compared to δ_C 187.6) and not the isomer **22**, thus showing conclusively that it is the intermediate **9** or its diradical analogue rather than **10** which reacts with **11** to give **6**.



4 **20** **21** **22**

Scheme 6

We cannot however exclude the possibility that, in the absence of added **11**, formation of **6** is by dimerisation of an intermediate, probably **9**, to give **8** which then loses CO. Whichever mechanism is operating, it should be possible to trap the intermediates with other added dipolarophiles leading to new types of stabilised ylides and this is currently being examined.

Finally, in the course of this study we have become aware of conflicting information regarding the ^{13}C NMR spectrum of triphenylphosphoranylideneketene **11**. This compound was first reported by Birum and Matthews,[13,14] but was later obtained in a more convenient way by base-induced elimination of methanol

from methoxycarbonylmethylenetriphenylphosphorane as shown in Scheme 5.[8,9] There are three literature reports of its ^{13}C NMR spectrum and there is widespread agreement on the rather remarkable chemical shifts of the ketene carbons [δ_C –10.5 (d, *J* 189, P=C), 145.6 (d, *J* 43, P=C=C=O)]. The situation for the P-phenyl signals is however confused as summarised in Table 1 with erroneous data shaded. Analysis of the ^{13}C NMR spectra of nearly 200 stabilised triphenylphosphonium ylides,[1] shows that the P-phenyl signals form a regular pattern with the *ipso*-C having a large coupling constant to phosphorus of between 90 and 100 Hz, the *ortho*-C coming around 132-133 ppm with a coupling constant of 9–11 Hz, the *meta*-C coming around 128–129 ppm with a larger coupling constant of 12–13 Hz, and the *para*-C around 132 ppm with a coupling constant of 0–2 Hz. The main problem in correctly interpreting the spectrum of **11** is the close proximity of the *ortho* and *para* signals and partial or complete overlap of one half of the *ortho* doublet with the *para* singlet giving two apparent singlets. The previous reports have all made this mistake,[9,15,16] with two also interchanging the *ortho* and *meta* signals.[9,16] The corrected data as obtained in our work is shown and this agrees with the revised data newly acquired by one of the original authors.[17]

Table 1. ^{13}C NMR data for the P-phenyl group of **11**

Frequency	Solvent	*ipso*-C	*ortho*-C	*meta*-C	*para*-C	Ref.
100 MHz	$CDCl_3$	129.6 (d, J 98.5)	128.8 (d, J 12.9)	132.3 (s)	132.2 (s)	9
125 MHz	C_6D_6	129.6 (d, J 98)	132.3 (s)	128.8 (d, J 13)	132.2 (s)	15
100 MHz	$CDCl_3$	129.6 (d, J 98.7)	128.8 (d, J 12.9)	132.3 (s)	132.2 (s)	16
75 MHz	$CDCl_3$	129.6 (d, J 99)	132.2 (d, J 11)	128.8 (d, J 13)	132.1 (s)	this work
125 MHz	$CDCl_3$	129.6 (d, J 99)	132.3 (d, J 11)	128.9 (d, J 13)	132.2 (s)	17

Conclusions

The result of the isotopic labeling experiment indicates that formation of the trioxo bis(ylide) **6** from both **4** and **5** proceeds by initial loss of CO_2 or COS respectively to give ylide **7**. This undergoes both loss of CO to afford the ketene ylide **11** and ring-opening to the dipolar species **9** which then combine in a cycloaddition reaction to form **6**. Purely thermal cyclotrimerisation of the ketene ylide **11** to give **12** has been observed and correct interpretation of the ^{13}C NMR data for **11** shows this to be consistent with the usual pattern of chemical shifts and P–C coupling constants for triphenylphosphonium ylides.

Experimental Section

General. Melting points were determined using a Reichert hot-stage microscope and are uncorrected. NMR spectra were recorded using a Varian Gemini 2000 instrument at 300 MHz for ^{1}H, 75 MHz for ^{13}C, and 121 MHz for ^{31}P. All spectra were recorded on solutions in $CDCl_3$ with internal Me_4Si as reference for ^{1}H and ^{13}C and external H_3PO_4 as reference for ^{31}P. Chemical shifts (δ) are given in ppm to high frequency from the reference and coupling constants (*J*) are in Hz. Flash vacuum pyrolysis was performed using the set-up previously described.[18] Compounds **4**,[4] **5**,[5] and **11**[8,9] were prepared by the published methods.

Flash Vacuum Pyrolysis of 4. FVP of **4** (36.5 mg) at 400 °C and 10^{-2} Torr gave a brown solid at the furnace exit that was mainly Ph_3PO (δ_P +29.2) and gaseous products in the cold trap that condensed as a white solid. Addition of methanol to the cold trap followed by warming to RT did not result in trapping of any reactive products and no phosphorus compounds were present.

Repeat FVP of **4** (320 mg) at 200 °C and 10^{-2} Torr gave a white solid at the furnace exit that proved to be a 5:3 mixture of Ph_3PO and Ph_3P (δ_P –5.0). In the inlet tube a pink solid was left which proved to be 3,5-bis(triphenyphosphoranylidene)cyclopentane-1,2,4-trione **6** (22 mg, 9%). ^{1}H NMR: δ_H 7.40–7.75 (30H, m). ^{13}C NMR: δ_C 67.6 (dd, *J* 112, 4, P=C), 124.6 (d, *J* 92, C-1 of Ph), 128.5 (d, *J* 13, C-3 of Ph), 132.3 (d, *J* 2, C-4 of Ph), 134.1 (d, *J* 11, C-2 of Ph), 187.6 (dd, *J* 20, 6, 1,2-CO), 196.4 (t, *J* 10, 4-CO). ^{31}P NMR: δ_P +9.0 (Lit.,[7] +8.8).

Flash Vacuum Pyrolysis of 5. FVP of **5** (29 mg) at 600 °C and 10^{-2} Torr gave a white solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to consist of small amounts of Ph_3PO, Ph_3PS (δ_P +43.6) and mainly ketenylidenetriphenylphosphorane **11** (δ_P +5.7).

Solution Pyrolysis of 4. A solution of **4** (44 mg) in diphenyl ether (2 mL) was heated under reflux for 30 min. The solvent was removed by kugelrohr distillation to leave a dark coloured residue shown by ^{1}H and ^{31}P NMR to consist mainly of bis(ylide) **6** together with a little Ph_3PO.

Solution Pyrolysis of 5. A solution of **5** (20 mg) in diphenyl ether (1 mL) was heated under reflux for 4 h. The solvent was removed by Kugelrohr distillation to leave a dark coloured residue shown by ^{1}H and ^{31}P NMR to consist mainly of bis(ylide) **6** together with a little Ph_3PO.

Neat Pyrolysis of 4. A sample of **4** (20 mg) was heated in a kugelrohr distillation apparatus at 250 °C for 1.5 h. The resulting dark coloured solid was shown by ^{1}H and ^{31}P NMR to consist mainly of bis(ylide) **6**.

Neat Pyrolysis of 5. A sample of **5** (10 mg) was heated in a kugelrohr distillation apparatus at 250 °C for 3 h. The resulting dark coloured solid was shown by ^{1}H and ^{31}P NMR to consist mainly of unchanged **5**.

Solution Pyrolysis of 4 and 11 Together. A solution of **4** (40 mg, 0.11 mmol) and **11** (32 mg, 0.11 mmol) in diphenyl ether (1 mL) was heated under reflux for 2 h. The resulting dark coloured solution was shown by ^{31}P NMR to contain **6** (20%) in addition to Ph_3PO and Ph_3P.

Solution Pyrolysis of 11. A solution of **11** (46 mg) in diphenyl ether (1.5 mL) was heated under reflux for 30 min. The dark solution was shown by ^{31}P NMR to contain Ph_3PO, Ph_3P and 2,4,6-tris(triphenylphosphoranylidene)cyclohexane-1,3,5-trione **12** (δ_P +13.9).

Neat Pyrolysis of 11. Compound **11** (250 mg) was heated in a kugelrohr distillation apparatus at 200 °C for 3 h. After this time a vacuum was applied and a colourless oil distilled off which proved to be Ph_3PO. The dark residue was mainly 2,4,6-tris(triphenylphosphoranylidene)cyclohexane-1,3,5-trione **12** (60%). ^{13}C NMR: δ_C 74.3 (dt, *J* 116, 10, P=C), 127.6 (d, *J* 12, C-3 of Ph), 128.3 (d, *J* 91, C-1 of Ph), 130.4 (C-4 of Ph), 133.6 (d, *J* 10, C-2 of Ph), 184.3 (CO). ^{31}P NMR: δ_P +13.4 (Lit.,[7] +13.7).

(Methoxycarbonylmethyl)tri-*p*-tolylphosphonium bromide (15). To a stirred solution of tri-*p*-tolylphosphine[11] (2.0 g, 6.6 mmol) in dry toluene (40 mL) a solution of methyl bromoacetate (1.0 g, 6.6.mmol) in dry toluene (20 mL) was added dropwise. After stirrring at RT for 18 h, the resulting white precipitate was filtered off and washed with diethyl ether to give the product (2.6 g, 87%) as a white powder, mp 187–189 °C. ^{1}H NMR: δ_H 2.48 (9H, s, Me), 3.59 (3H, s, OMe), 5.37 (2H, d, *J* 12, P-CH_2), 7.39–7.50 (6H, m), 7.66–7.80 (6H, m). ^{13}C NMR: δ_C 21.8 (Me), 33.0 (d, *J* 58, P-CH_2), 53.2 (OMe), 114.6 (d, *J* 92, C-1 of Tol), 130.9 (d, *J* 14, C-3 of Tol), 133.7 (d, *J* 11, C-2 of Tol), 146.3 (d, *J* 3, C-4 of Tol), 165.2 (C=O). ^{31}P NMR: δ_P +20.2.

(Methoxycarbonylmethylene)tri-*p*-tolylphosphorane (16). A solution of the salt **15** (2.5 g, 5.5 mmol) in water (20 mL) was stirred rapidly while NaOH (0.22 g, 5.5 mmol) was added. The resulting mixture was extracted with ethyl acetate (3 x 10 mL) and the extract was dried and evaporated to give the title compound (1.6 g, 77%) as a yellow solid, mp 85–87 °C. IR (Nujol, ν_{max}, cm^{-1}): 1728, 1271, 1118, 808. ^{1}H NMR: δ_H 2.38 (9H, s, Me),

3.40 (1H, br s, =CH), 3.52 (3H, s, OMe), 7.20–7.36 (6H, m), 7.48–7.65 (6H, m). ^{13}C NMR: δ_C 21.4 (Me), 30.4 (d, *J* 119, P=C), 49.8 (OMe), 123.5 (d, *J* 96, C-1 of Tol), 129.4 (d, *J* 13, C-3 of Tol), 132.8 (d, *J* 10, C-2 of Tol), 142.5 (C-4 of Tol), 170.8 (d, *J* 11, C=O). ^{31}P NMR: δ_P +16.7. MS (CI) *m/z* 377 (M^+, 34%), 361 (6), 345 (24), 321 (100), 305 (11). HRMS: $C_{24}H_{26}O_2P$ (M+H) requires 377.1670. Found: 377.1665.

Tri-*p*-tolylphosphoranylideneketene (17). A solution of ylide **16** (0.95 g, 2.5 mmol) was stirred in dry toluene (10 mL) under nitrogen while sodium amide (0.34 g, 8.7 mmol) was added. The mixture was heated under reflux under nitrogen for 24 h then cooled and filtered under nitrogen. Evaporation of the filtrate gave a solid containing tri-p-tolylphosphine oxide (δ_P +29.4) and the title product (0.4 g, 46%). ^{13}C NMR: δ_C 142.6 (d, *J* 39, P=C=C=O). ^{31}P NMR: δ_P +5.3.

Attempted Pyrolysis of 17 with 4 or on its own. All attempts at solution pyrolysis of **17**, either with or without added **4**, in boiling diphenyl ether, as well as neat pyrolysis of **17** in a kugelrohr oven at 170 °C, gave tri-*p*-tolylphosphine oxide as the only significant phosphorus-containing product.

^{13}C-Labelled Methyl Bromoacetate. Thionyl chloride (9.3 g, 5.7 mL, 78 mmol) was added dropwise to a solution of 20% ^{13}C-CO-labelled bromoacetic acid (5.0 g, 36 mmol) in methanol (50 mL) and the mixture was stirred at RT for 2 h. Evaporation followed by distillation at atmospheric pressure gave the product as a colourless liquid, bp 135–140 °C. ^{1}H NMR: δ_H 2.92 (3H, s, OMe), 2.95 (2H, s, CH_2). ^{13}C NMR: δ_C 25.5 (CH_2), 53.2 (OMe), 167.7 (CO, 20 x enhanced compared to unlabelled material).

^{13}C-CO Labelled (Methoxycarbonylmethylene)triphenylphosphonium Bromide (18). A solution containing labelled methyl bromoacetate (5.0 g, 33 mmol) and triphenylphosphine (8.56 g, 33 mmol) in dry toluene (30 mL) was stirred at RT for 48 h. The resulting solid was filtered off and dried to give the title product (11.03 g, 81%) as colourless crystals, mp 161–162 °C (Lit.,[19] 163 °C). ^{13}C NMR: δ_C 32.7 (d, *J* 57, CH_2), 53.2 (OMe), 117.5 (d, *J* 89, C-1 of Ph), 130.1 (d, *J* 13, C-3 of Ph), 133.7 (d, *J* 11, C-2 of Ph), 135.0 (d, *J* 2, C-4 of Ph), 164.8 (d, *J* 3, C=O, 20 x enhanced). ^{31}P NMR: δ_P +22.8 (Lit.,[20] +20.3).

20% ^{13}C-CO Labelled (Methoxycarbonylmethylene)triphenylphosphorane (19). A solution of the salt **18** (4.0 g, 9.6 mmol) in water (30 mL) was stirred rapidly while NaOH (0.39 g, 9.6 mmol) was added. The resulting mixture was extracted with ethyl acetate (3 x 10 mL) and the extract was dried and evaporated to give the title compound (2.6 g, 81%) as a white solid, mp 163–164 °C (Lit.,[19] 162–163 °C). ^{13}C NMR: δ_C 29.7 (d, *J* 127, P=C), 49.6 (OMe), 127.7 (d, *J* 91, C-1 of Ph), 128.6 (d, *J* 12, C-3 of Ph), 131.8 (C-4 of Ph), 132.8 (d, *J* 10, C-2 of Ph), 171.5 (d, *J* 12, C=O, 20 x enhanced). ^{31}P NMR: δ_P +18.2 (Lit.,[13] +17.6).

20% ^{13}C-CO Labelled Triphenylphosphoranylideneketene (20). A solution of labelled ylide **19** (1.4 g, 4.2 mmol) was stirred in dry toluene (7 mL) under nitrogen while sodium amide (0.40 g, 10 mmol) was added. The mixture was heated under reflux under nitrogen for 48 h then cooled and filtered under nitrogen. Evaporation of the filtrate gave a solid containing a 1:2 mixture of triphenylphosphine oxide (δ_P +29.2) and the title product (0.63 g, 50%). ^{13}C NMR: δ_C –10.5 (d, *J* 189, P=C), 128.8 (d, *J* 13, C-3 of Ph), 129.6 (d, *J* 99, C-1 of Ph), 132.1 (C-4 of Ph), 132.2 (d, *J* 11, C-2 of Ph), 145.6 (d, *J* 43, P=C=C=O, 20 x enhanced). ^{31}P NMR: δ_P +5.6 (Lit.,[21] +5.4).

Solution Pyrolysis of 4 and 20 Together. A solution of **4** (210 mg, 0.56 mmol) and **20** (170 mg, 0.56 mmol) in diphenyl ether (4 mL) was heated under reflux for 2 h. The resulting dark coloured solution was shown by ^{31}P NMR to contain (a labelled version of) **6** (δ_P +9.1) in addition to Ph_3PO and Ph_3P. In the carbonyl region of the ^{13}C NMR spectrum the signal at δ_C 196.0 (t, *J* 9, 4-CO) showed a 20 x enhancement compared to the signal at δ_C 187.2 (dd, *J* 20, 6, 1,2-CO), i.e. corresponding to structure **21** and not **22**.

Acknowledgements

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