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## FORMATION OF UNEXPECTED HETEROCYCLIC PRODUCTS FROM PYROLYSIS OF THIOCARBONYL STABILISED PHOSPHONIUM YLIDES

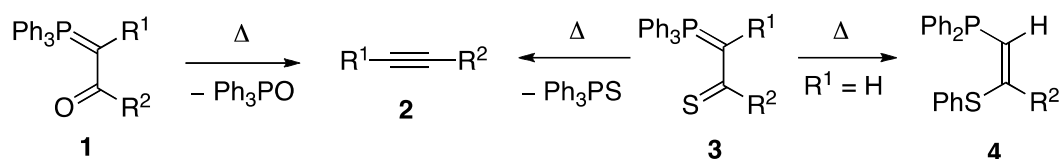
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**Abstract** – Chiral phthalimido thioxo-stabilised phosphonium ylides, prepared starting from (*S*)-alanine and (*S*)-phenylalanine, undergo intramolecular Wittig reaction upon pyrolysis leading to the previously unknown pyrrolo[2,1-*a*]isoindol-5-one-2-thiones, rather than the expected P to S migration of a phenyl group. Pyrolysis of thioxo-stabilised ylides with three different groups on phosphorus gave some evidence of the required migration, but led in one case to unexpected formation of a 1,4-benzoxaphosphinium salt.

## INTRODUCTION

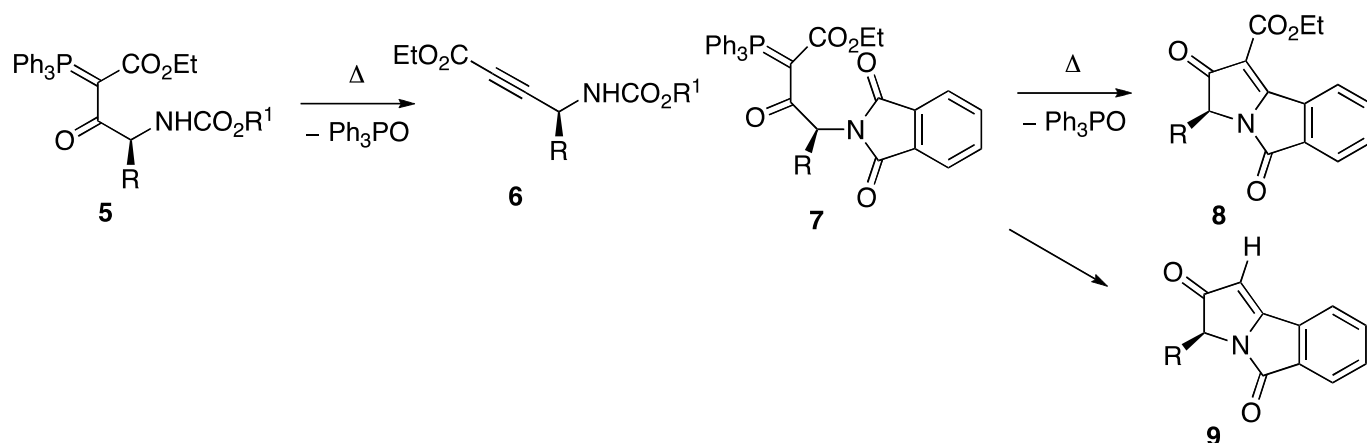
Thermal extrusion of Ph<sub>3</sub>PO from oxo-stabilised phosphonium ylides **1** provides a useful route for synthesis of substituted alkynes **2**,<sup>1</sup> and has recently been used to access such diverse systems as acetylenic amino acid derivatives,<sup>2</sup> rings fused carbazoles,<sup>3</sup> and polycyclic thieno[2,3-*b*]pyridine derivatives (Scheme 1).<sup>4</sup> In contrast, the corresponding reaction of thioxo-stabilised ylides **3** has been much less studied, but we recently reported that, while most such compounds undergo extrusion of Ph<sub>3</sub>PS to give alkynes **2**, those with R<sup>1</sup> = H instead undergo rearrangement with transfer of one phenyl group to afford the *Z*-1-sulfanyl-2-phosphanylalkenes **4**.<sup>5</sup> Since these were shown to be potentially useful hemi-labile ligands for transition metals, we have investigated the formation of chiral analogues which might be useful in asymmetric catalysis. In this paper, two separate approaches are described: pyrolysis of thioxo-stabilised ylides bearing an amino acid-derived chiral auxiliary, and pyrolysis of thioxo-stabilised ylides derived from *P*-stereogenic phosphines. In each case unexpected thermal processes intervened leading to unusual and interesting heterocyclic products.



**Scheme 1.** Previous thermolysis of oxo- and thio-ylides

**RESULTS AND DISCUSSION**

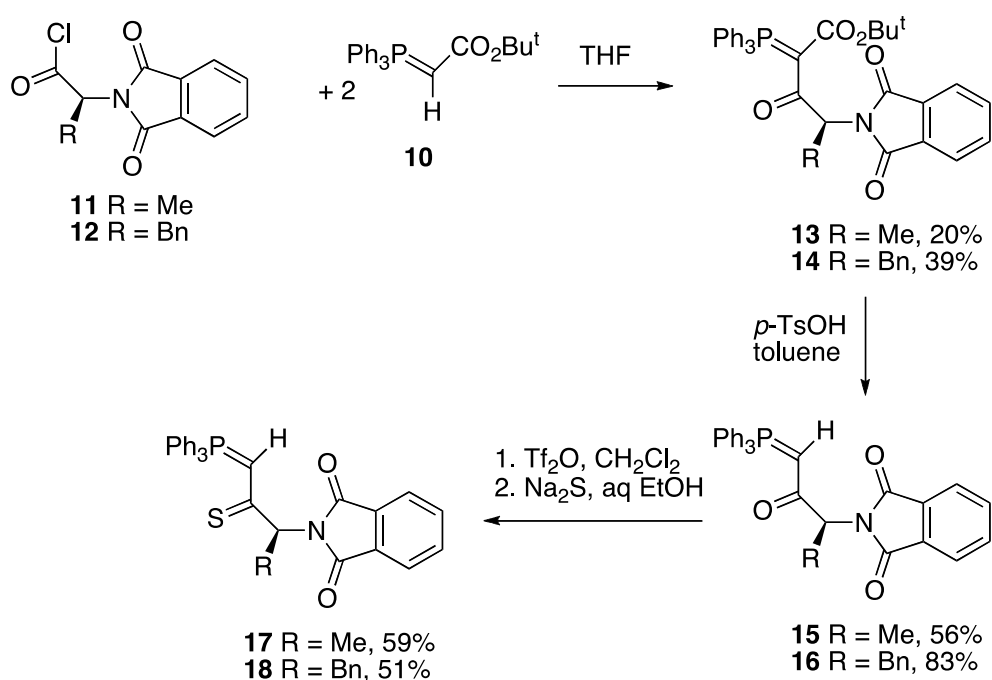
The first approach was based on the fact that suitably *N*-protected amino acid derivatives can be used to acylate phosphonium ylides and the resulting oxo-stabilised ylides undergo thermal extrusion of  $\text{Ph}_3\text{PO}$  to give chiral products without significant racemisation. Thus, we showed previously that *N*-alkoxycarbonyl ylides **5** could be prepared and converted into the alkynes **6** using flash vacuum pyrolysis (FVP) at 600 °C (Scheme 2).<sup>2,6</sup> Cyclic amino acid-derived stabilised ylides were also prepared similarly.<sup>7</sup> In an earlier study, the phthalimidoacyl ylides **7** were prepared, but unexpectedly they underwent an intramolecular Wittig reaction upon FVP at 500 °C to give the pyrroloisindole-diones **8**, while at the higher temperature of 750 °C, the ester group was lost to afford products **9**.<sup>8</sup> We have also observed the competitive intramolecular extrusion of  $\text{Ph}_3\text{PO}$  between an ylide function and  $\beta$  and  $\delta$  carbonyl groups, leading in the latter case to transient formation of a cyclobutene.<sup>9,10</sup>



**Scheme 2.** Previous thermolysis of aminoacyl ylides

Although it was expected that the corresponding thio-ylides would show similar behaviour, no such compounds appear to have been reported before. Our planned synthesis relied on the fact that stabilised ylides bearing an  $\alpha$ -*tert*-butoxycarbonyl group undergo ready loss of isobutene and  $\text{CO}_2$  upon treatment with *p*-toluenesulfonic acid.<sup>11</sup> We thus started by reacting two equivalents of *tert*-butyl triphenylphosphoranylideneacetate **10** with the phthalimidoacyl chlorides **11** and **12**, prepared, respectively, by successive treatment of (*S*)-alanine and (*S*)-phenylalanine with phthalic anhydride

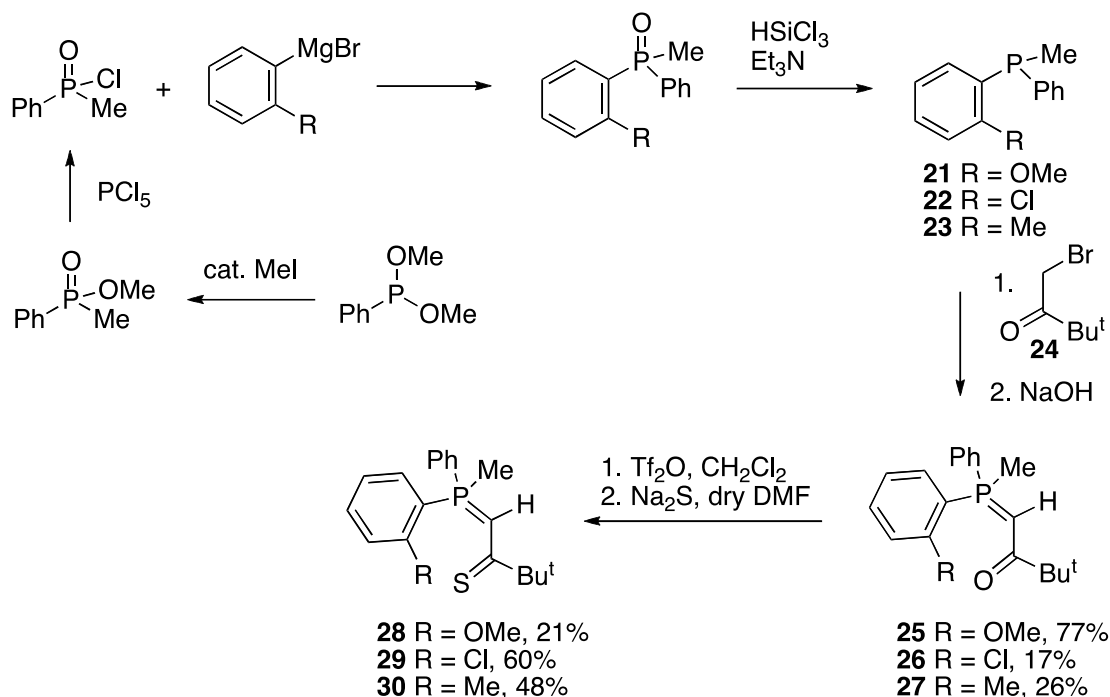
followed by thionyl chloride (Scheme 3). This gave the expected ylide products **13** and **14** as stable crystalline solids in low to moderate yield after chromatographic purification. As for all ylides described in this paper, their structure was readily confirmed from the highly informative  $^{13}\text{C}$  NMR spectra with phosphorus coupling to almost all signals. The removal of the *tert*-butoxycarbonyl groups was now carried out using the reported method,<sup>11</sup> but replacing benzene with the less harmful toluene, to give the ylides **15** and **16** in moderate to good yield. In our previous work,<sup>5</sup> conversion of the C=O into C=S was achieved directly by treatment with Lawesson's reagent,<sup>12</sup> however for these more sensitive compounds this was not suitable. Instead we reverted to the two-step method of Bestmann,<sup>13</sup> involving reaction with trifluoromethanesulfonic anhydride to form the *O*-sulfonylphosphonium triflate, then evaporation and treatment of the residue *in situ* with sodium sulfide in aqueous ethanol. This afforded the target thioxo-stabilised ylides **17** and **18** in acceptable yield.



**Scheme 3.** Synthetic route to phthalimido thioxo-stabilised ylides

These were now subjected to FVP using a temperature of 650 °C and a pressure of  $10^{-2}$  Torr leading to complete reaction and collection of solid products in the cold trap, which proved in each case to be a mixture of  $\text{Ph}_3\text{PO}$  and a new product readily separated from it by chromatography. These were identified as the pyrrolo[2,1-*a*]isoindol-5-one-2-thiones **19** and **20** formed in moderate yield, which appear to be a previously unknown compound type.

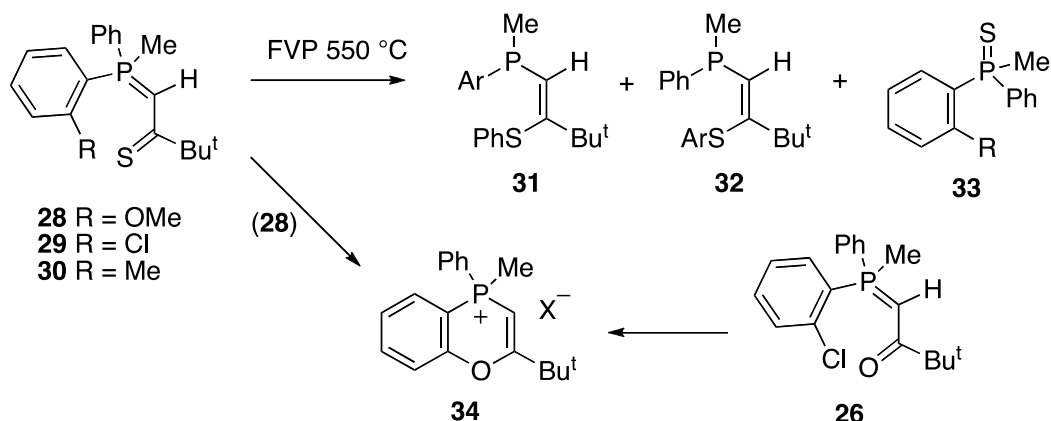




**Scheme 5.** Synthetic route to thioxo-stabilised ylides

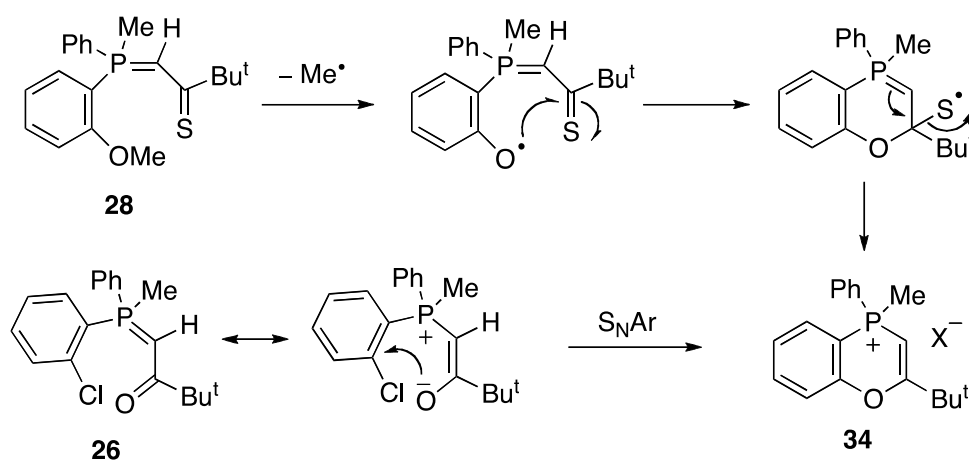
When these ylides were subjected to FVP at  $10^{-2}$  Torr and 550 or 600 °C, the products collected in the cold trap were rather complex mixtures, which did however show some indication of the desired process having occurred (Scheme 6). Thus for **28** a component with a  $^{31}\text{P}$  NMR signal at  $-55.5$  was present consistent with product **31** or **32**, while for **30** two separate products with  $^{31}\text{P}$  NMR signals at  $-39.9$  and  $-49.3$  in a 2:1 ratio also seemed likely to be the rearrangement products. However in each case these were accompanied by the phosphine sulfide **33** and various other products, meaning that the reactions were unlikely to be of much preparative value. When the residue in the inlet tube was examined however a more interesting result was obtained. The NMR data for the residue in the inlet after FVP of **28** at 550 °C was consistent with the 1,4-benzoxaphosphininium salt structure **34** where the nature of the counterion is unclear. A very similar product was obtained as the involatile residue left when the 2-chlorophenyl oxo-stabilised ylide **26** was subjected to FVP.

The  $^{31}\text{P}$  NMR shift around  $-10$  ppm is in reasonable agreement with values previously determined for similar 1,4-oxaphosphininium salts,<sup>17,18</sup> and both the chemical shift (6.2–6.3 ppm) and coupling constant ( $J = 8$  Hz) for H-3 are in excellent agreement with literature values.<sup>18</sup> Perhaps the most convincing confirmation of the structure comes from the  $^{13}\text{C}$  NMR spectra where signals for the four different carbons directly attached to phosphorus are especially prominent [123.7 (d,  $J = 93$  Hz, Ph C-1), 100.9 (d,  $J = 89$  Hz, C-4a), 74.9 (d,  $J = 89$  Hz, CH, C-3), 12.9 (d,  $J = 61$  Hz, PMe)].



**Scheme 6.** Pyrolysis of thioxo-stabilised ylides

In terms of the mechanism for these processes, we postulate initial loss of a methyl radical from **28**, a reaction commonly observed under FVP conditions for a wide range of 2-methoxyphenylphosphonium ylides,<sup>19</sup> followed by 6-*exo-trig* cyclisation onto the thiocarbonyl function (Scheme 7). The form in which sulfur is lost and the nature of the resulting counterion is unclear.



**Scheme 7.** Proposed mechanisms for benzoxaphosphinonium salt formation

In the case of **26**, the phosphonium enolate resonance form which is a major contributor to the ylide structure simply undergoes an intramolecular  $S_NAr$  reaction to afford the benzoxaphosphinonium chloride.

## EXPERIMENTAL

Melting points were recorded on a Reichert hot-stage microscope and are uncorrected. IR spectra were determined on a Perkin-Elmer 1710 spectrometer as Nujol mulls or thin films. All NMR spectra were obtained using a Varian Gemini 2000 spectrometer, at 300 MHz for  $^1H$ , 121 MHz for  $^{31}P$ , and 75 MHz for

$^{13}\text{C}$ , and are reported in ppm to high frequency of TMS as internal standard for H and C and relative to external 85%  $\text{H}_3\text{PO}_4$  for P. Spectra were recorded in  $\text{CDCl}_3$  unless otherwise stated. Mass spectra were recorded using an AEI Kratos MS-50 spectrometer using EI (70 eV) or, where noted, CI (isobutane). Elemental analysis was performed using a Carlo-Erba 1106 analyser.

For flash vacuum pyrolysis (FVP), the sample was volatilised from a tube in a Büchi Kugelrohr oven through a  $30 \times 2.5$  cm horizontal fused quartz tube. This was heated externally by a Carbolite Eurotherm tube furnace MTF-12/38A, the temperature being monitored by a Pt/Pt-13%Rh thermocouple situated at the centre of the furnace. The products were collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of  $10^{-2}$  Torr by an Edwards Model E2M5 high capacity rotary oil pump, the pressure being measured by a Pirani gauge situated between the cold trap and the pump. Under these conditions the contact time in the hot zone was estimated to be 10 ms.

### Starting Materials

*tert*-Butyl triphenylphosphoranylideneacetate **10**<sup>11</sup> was prepared by reacting *tert*-butyl chloroacetate with triphenylphosphine in toluene to give the phosphonium salt (80%) and then treating this with sodium hydroxide (89%). (2*S*)-2-Phthalimidopropionyl chloride **11**<sup>8</sup> and (2*S*)-3-phenyl-2-phthalimidopropionyl chloride **12**<sup>8</sup> were prepared, respectively, from (*S*)-alanine and (*S*)-phenylalanine by first melting a mixture of the amino acids with phthalic anhydride, heating for 4 h and recrystallising the product from water, then treatment with thionyl chloride followed by evaporation. The unsymmetrical tertiary phosphines (2-methoxyphenyl)methylphenylphosphine **21**, (2-chlorophenyl)methylphenylphosphine **22** and (2-methylphenyl)methylphenylphosphine **23** were prepared by the multi-step method of Gilheaney and co-workers<sup>15</sup> as shown in Scheme 5.

### Preparation of *tert*-butyl (4*S*)-3-oxo-4-phthalimido-2-triphenylphosphoranylidene-pentanoate **13**

A solution of *tert*-butyl triphenylphosphoranylideneacetate **10** (5.57 g, 16 mmol) in dry THF (50 mL) was stirred while a solution of (2*S*)-2-phthalimidopropionyl chloride **11** (2.25 g, 8 mmol) in dry THF (25 mL) was added and the mixture was heated under reflux for 4 h. The mixture was cooled and filtered. Evaporation of the filtrate followed by column chromatography of the residue ( $\text{SiO}_2$ , EtOAc) and recrystallisation from petroleum/EtOAc gave the product **13** (0.90 g, 20%) as colourless crystals; mp 208–210 °C;  $[\alpha_D]$  +3.75 (*c* 1.0,  $\text{CH}_2\text{Cl}_2$ ); IR 1709, 1668, 1592, 1387, 1307, 1163, 1078, 925, 722  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.7–7.5 (m, 10H), 7.5–7.3 (m, 9H), 6.02 (q,  $J = 7$  Hz, 1H), 1.95 (d,  $J = 7$  Hz, 3H), 1.05 (s, 9H);  $^{13}\text{C}$  NMR  $\delta$  192.2 (d,  $J = 4$  Hz, CO), 168.7 (N-CO), 166.7 (d,  $J = 14$  Hz, COO), 133.2 (2CH), 133.0 (d,  $J = 10$  Hz, PPh C-2), 132.5 (2C), 131.5 (d,  $J = 3$  Hz, PPh C-4), 128.5 (d,  $J = 13$  Hz, PPh C-3), 126.6 (d,  $J = 93$  Hz, PPh C-1), 122.8 (2CH), 78.8 ( $\text{CMe}_3$ ), 54.2 (d,  $J = 9$  Hz,  $\text{CHMe}$ ), 28.1 ( $\text{CMe}_3$ ), 16.0 ( $\text{CHMe}$ ) [ylide

C not apparent];  $^{31}\text{P}$  NMR  $\delta$  +18.9; MS (CI)  $m/z$  578 ( $\text{M}+\text{H}^+$ , 5), 364 (19), 319 (8), 301 (5), 279 (33), 263 (100). Anal. Calcd for  $\text{C}_{35}\text{H}_{32}\text{NO}_5\text{P}$ : C, 72.78; H, 5.58; N, 2.42. Found: 73.10; H, 5.72; N, 2.66.

#### Preparation of *tert*-butyl (4*S*)-3-oxo-5-phenyl-4-phthalimido-2-triphenylphosphoranylidene-pentanoate **14**

The same method as for **13** using *tert*-butyl triphenylphosphoranylideneacetate **10** and (2*S*)-3-phenyl-2-phthalimidopropionyl chloride **12** (2.47 g, 8 mmol) gave the product **14** (1.81 g, 39%) as colourless crystals; mp 200–202 °C;  $[\alpha_{\text{D}}]$  –1.30 ( $c$  1.0,  $\text{CH}_2\text{Cl}_2$ ); IR 1711, 1646, 1624, 1571, 1440, 1326, 1176, 1108, 1090, 729, 693  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.8–7.6 (m, 8H), 7.5–7.3 (m, 12H), 7.2–7.0 (m, 4H), 6.35 (dd,  $J$  = 12, 4 Hz, 1H), 3.90 (half AB pattern of d,  $J$  = 14, 12 Hz, 1H), 3.85 (half AB pattern of d,  $J$  = 14, 4 Hz, 1H), 1.05 (s, 9H);  $^{13}\text{C}$  NMR  $\delta$  190.0 (d,  $J$  = 4 Hz, CO), 168.8 (N-CO), 166.8 (d,  $J$  = 14 Hz, COO), 139.4 (C), 133.1 (2CH), 133.1 (d,  $J$  = 10 Hz, PPh C-2), 132.2 (2C), 131.6 (d,  $J$  = 3 Hz, PPh C-4), 129.1 (2CH), 128.5 (d,  $J$  = 13 Hz, PPh C-3), 128.1 (2CH), 126.6 (d,  $J$  = 93 Hz, PPh C-1), 126.0 (CH), 122.8 (2CH), 78.8 ( $\text{CMe}_3$ ), 60.5 (d,  $J$  = 9 Hz,  $\text{CHMe}$ ), 34.8 ( $\text{CH}_2\text{Ph}$ ) 28.1 ( $\text{CMe}_3$ ) [ylide C not apparent];  $^{31}\text{P}$  NMR  $\delta$  +18.9; MS (CI)  $m/z$  653 ( $\text{M}^+$ , 2), 386 (10), 364 (29), 338 (27), 320 (21), 294 (25), 279 (80), 263 (64), 196 (6), 89 (100). Anal. Calcd for  $\text{C}_{41}\text{H}_{36}\text{NO}_5\text{P}$ : C, 75.33; H, 5.55; N, 2.14. Found: 75.64; H, 5.29; N, 2.10.

#### Preparation of (3*S*)-2-oxo-3-phthalimidobutylidene-triphenylphosphorane **15**

A solution of ylide **13** (0.72 g, 1.23 mmol) and *p*-toluenesulfonic acid (0.36 g, 1.85 mmol) in toluene (50 mL) was heated under reflux for 3 h. The solution was cooled and added to a mixture of aqueous NaOH (2 M) and EtOAc. Separation and drying of the organic layer followed by evaporation gave the product **15** (0.34 g, 56%) as a colourless solid; mp 214–216 °C;  $[\alpha_{\text{D}}]$  –1.60 ( $c$  1.0,  $\text{CH}_2\text{Cl}_2$ ); IR 1771, 1706, 1603, 1378, 1225, 1121, 881, 723, 680  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.80 (m, 2H) 7.7–7.6 (m, 6H), 7.6–7.4 (m, 9H), 7.3–7.2 (m, 2H), 5.00 (q,  $J$  = 6 Hz, 1H), 3.75 (br s, 1H, P=CH), 1.80 (d,  $J$  = 6 Hz, 3H);  $^{13}\text{C}$  NMR  $\delta$  187.6 (CO), 168.3 (N-CO), 133.4 (2CH), 133.1 (d,  $J$  = 10 Hz, PPh C-2), 132.5 (2C), 131.9 (PPh C-4), 128.7 (d,  $J$  = 13 Hz, PPh C-3), 126.8 (d,  $J$  = 91 Hz, PPh C-1), 122.9 (2CH), 53.0 (d,  $J$  = 15 Hz, CH), 48.9 (d,  $J$  112 Hz, P=C), 16.2 (Me);  $^{31}\text{P}$  NMR  $\delta$  +17.6; MS (CI)  $m/z$  477 ( $\text{M}^+$ , 5), 317 (6), 279 (100), 263 (25), 200 (46). Anal. Calcd for  $\text{C}_{30}\text{H}_{24}\text{NO}_3\text{P}$ : C, 75.46; H, 5.07; N, 2.93. Found: 75.73; H, 5.14; N, 2.55.

#### Preparation of (3*S*)-2-oxo-4-phenyl-3-phthalimidobutylidene-triphenylphosphorane **16**

The same method as for **15** using ylide **14** (0.26 g, 0.409 mmol) and *p*-toluenesulfonic acid (0.12 g, 0.614 mmol) gave the product **16** (0.20 g, 83%) as a colourless solid; mp 183–185 °C;  $[\alpha_{\text{D}}]$  +4.2 ( $c$  1.0,  $\text{CH}_2\text{Cl}_2$ ); IR 1770, 1711, 1378, 1107, 718  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.75–7.40 (m, 16H), 7.30–7.05 (m, 8H), 5.20 (t,  $J$  = 8 Hz, 1H), 3.80 (br s, 1H, P=CH), 3.70 (d,  $J$  = 8 Hz, 2H);  $^{13}\text{C}$  NMR  $\delta$  186.5 (CO), 168.4 (N-CO), 139.2 (C), 133.4 (2CH), 133.1 (d,  $J$  = 10 Hz, PPh C-2), 132.0 (PPh C-4), 131.6 (2CH), 128.9 (d,  $J$  = 13 Hz, PPh C-3), 128.5 (CH), 128.4 (2CH), 126.9 (C), 126.7 (d,  $J$  = 85 Hz, PPh C-1), 123.0 (2CH), 58.9 (d,



$J = 15$  Hz, CH), 49.6 (d,  $J$  111 Hz, P=C), 35.1 (CH<sub>2</sub>); <sup>31</sup>P NMR  $\delta$  +17.6; MS (CI)  $m/z$  554 (M+H<sup>+</sup>, 1), 294 (15), 279 (100), 263 (29), 203 (11). Anal. Calcd for C<sub>36</sub>H<sub>28</sub>NO<sub>3</sub>P: C, 78.10; H, 5.10; N, 2.53. Found: 77.64; H, 4.78; N, 2.35.

#### Preparation of (3*S*)-2-thioxo-3-phthalimidobutylidenetriphenylphosphorane 17

A solution of ylide **15** (2.0 g, 4.2 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was stirred while trifluoromethanesulfonic anhydride (1.18 g, 4.2 mmol) was added dropwise. The mixture was stirred under N<sub>2</sub> for 15 h and the evaporated. The residue was dissolved in EtOH (50 mL) and a solution of sodium sulfide nonahydrate (1.51 g, 6.3 mmol) in water (50 mL) was added. After stirring for 12 h, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). Drying and evaporation of the extract gave the product **17** as a yellow powder (1.22 g, 59%); mp 204–205 °C; [ $\alpha$ <sub>D</sub>] –0.9 ( $c$  1.0, CH<sub>2</sub>Cl<sub>2</sub>); IR 1703, 1103, 720 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.9–7.3 (m, 19H), 5.32 (d,  $J = 40$  Hz, 1H, P=CH), 5.28 (q,  $J = 7$  Hz, 1H), 1.92 (d,  $J = 7$  Hz, 3H); <sup>13</sup>C NMR  $\delta$  200.0 (CS), 168.3 (N-CO), 133.4 (2CH), 133.3 (d,  $J = 9$  Hz, PPh C-2), 133.0 (2C), 132.2 (PPh C-4), 128.8 (d,  $J = 13$  Hz, PPh C-3), 124.4 (d,  $J = 93$  Hz, PPh C-1), 123.0 (2CH), 82.3 (d,  $J$  118 Hz, P=C), 57.8 (d,  $J = 17$  Hz, CH), 18.5 (Me); <sup>31</sup>P NMR  $\delta$  +8.6; MS (CI)  $m/z$  [M<sup>+</sup> not apparent], 291 (6), 279 (100), 263 (15), 220 (7). Anal. Calcd for C<sub>30</sub>H<sub>24</sub>NO<sub>2</sub>PS: C, 73.00; H, 4.90; N, 2.84. Found: 71.23; H, 4.80; N, 2.67.

#### Preparation of (3*S*)-2-thioxo-4-phenyl-3-phthalimidobutylidenetriphenylphosphorane 18

The same method as for **17** using ylide **16** (1.3 g, 2.4 mmol), trifluoromethanesulfonic anhydride (0.67 g, 2.4 mmol) and sodium sulfide nonahydrate (0.86 g, 3.6 mmol) gave the product **18** as a yellow powder (0.69 g, 51%); mp 217–218 °C; [ $\alpha$ <sub>D</sub>] –2.3 ( $c$  1.0, CH<sub>2</sub>Cl<sub>2</sub>); IR 1707, 1323, 1097, 722 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.7–7.4 (m, 20H), 7.3–7.0 (m, 4H), 5.50 (m, 1H), 5.30 (d,  $J = 40$  Hz, 1H, P=CH), 3.98 (dd,  $J = 14$ , 5 Hz, 1H, CH<sub>2</sub>), 3.75 (dd,  $J = 14$ , 8 Hz, 1H, CH<sub>2</sub>); <sup>13</sup>C NMR  $\delta$  198.2 (CS), 168.3 (N-CO), 139.1 (C), 133.4 (2CH), 133.3 (d,  $J = 10$  Hz, PPh C-2), 133.0 (2C), 132.3 (PPh C-4), 132.0 (2CH), 128.9 (d,  $J = 13$  Hz, PPh C-3), 128.2 (2CH), 126.1 (CH), 124.4 (d,  $J = 93$  Hz, PPh C-1), 123.0 (2CH), 83.0 (d,  $J$  116 Hz, P=C), 64.0 (d,  $J = 17$  Hz, CH), 37.6 (CH<sub>2</sub>); <sup>31</sup>P NMR  $\delta$  +8.6. Anal. Calcd for C<sub>36</sub>H<sub>28</sub>NO<sub>2</sub>PS: C, 75.90; H, 4.95; N, 2.46. Found: 76.22; H, 4.85; N, 2.63.

#### Preparation of (3*S*)-3-methyl-2-thioxo-2,3-dihydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one 19

The ylide **17** (0.45 g) was subjected to FVP at 650 °C and 10<sup>-2</sup> Torr. The material in the cold trap was dissolved out with CH<sub>2</sub>Cl<sub>2</sub> and shown by <sup>31</sup>P and <sup>1</sup>H NMR to consist of Ph<sub>3</sub>PO and a new compound. These were separated by column chromatography (SiO<sub>2</sub>, EtOAc) to give the product **19** (0.11 g, 55%) as light brown crystals; mp 114–116 °C; IR 1704, 1618, 1314, 1168, 892, 767, 696 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.85–7.80 (m, 1H), 7.75–7.70 (m, 1H), 7.70–7.60 (m, 2H), 5.95 (s, 1H), 4.27 (q,  $J = 7$  Hz, 1H), 1.59 (d,  $J = 7$  Hz, 3H); <sup>13</sup>C NMR  $\delta$  202.9 (CS), 165.1 (CO), 162.1 (C), 133.3 (CH), 133.0 (C), 132.6 (CH), 130.4 (C), 124.3 (CH), 124.2 (CH), 102.0 (CH), 57.3 (CH), 15.6 (Me); MS (CI)  $m/z$  200 (M<sup>+</sup>–Me, 100), 148

(10), 75 (6). HRMS Calcd for  $C_{11}H_6NOS$  ( $M^+-Me$ ): 200.0170. Found: 200.0176.

### Preparation of (3*S*)-3-benzyl-2-thioxo-2,3-dihydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one **20**

The ylide **18** (0.57 g) was subjected to FVP at 650 °C and  $10^{-2}$  Torr as described above to give, after chromatographic separation, the product **20** (0.15 g, 52%) as light brown crystals; mp 84–85 °C; IR 1718, 1620, 1076, 721  $cm^{-1}$ ;  $^1H$  NMR  $\delta$  7.90–7.85 (m, 1H), 7.75–7.65 (m, 1H), 7.65–7.60 (m, 2H), 7.15–7.05 (m, 5H), 5.80 (s, 1H), 4.60 (dd,  $J = 5, 3$  Hz, 1H), 3.73 (half AB pattern of d,  $J = 14, 5$  Hz,  $CH_2$ ), 3.56 (half AB pattern of d,  $J = 14, 3$  Hz,  $CH_2$ );  $^{13}C$  NMR  $\delta$  201.8 (CS), 167.3 (CO), 162.5 (C), 134.3 (C), 133.2 (CH), 132.5 (CH), 131.6 (C), 130.1 (C), 129.7 (2CH), 128.1 (2CH), 126.8 (CH), 124.3 (CH), 124.2 (CH), 103.2 (CH), 62.1 (CH), 35.1 ( $CH_2$ ); MS (CI)  $m/z$  200 ( $M^+-Me$ , 100), 148 (10), 75 (6). Anal. Calcd for  $C_{18}H_{13}NOS$ : C, 74.20; H, 4.50; N, 4.81. Found: 73.92; H, 4.83; N, 4.94.

### Preparation of 1-((2-methoxyphenyl)methyl(phenyl)phosphoranylidene)-3,3-dimethylbutan-2-one **25**

A solution of (2-methoxyphenyl)methylphenylphosphine **21** (0.94 g, 4 mmol) in dry toluene (25 mL) was stirred at rt while 1-bromo-3,3-dimethylbutan-2-one **24** (0.72 g, 4 mmol) was added dropwise. After the addition, the mixture was stirred for 12 h and the resulting oily solid was filtered off and washed with toluene. It was then dissolved in hot water (15 mL) and the resulting solution treated with NaOH (0.33 g, 8 mmol) dissolved in water (10 mL). The milky suspension was extracted with  $CH_2Cl_2$  ( $5 \times 30$  mL) and the combined extracts were dried and evaporated to give the product **25** (1.03 g, 77%) as a pale brown solid; mp 120–122 °C; IR 1590, 1522, 1275, 1107, 924, 752, 697  $cm^{-1}$ ;  $^1H$  NMR  $\delta$  7.74 (ddd,  $J = 15, 7.5, 1.5$  Hz, 1H), 7.62–7.40 (m, 6H), 7.13 (tdd,  $J = 7.5, 2, 1$  Hz, 1H), 6.93 (dd,  $J = 7.5, 5$  Hz, 1H), 3.68 (s, 3H, OMe), 3.43 (br s, 1H, P=CH), 2.44 (d,  $J = 15$  Hz, 3H, PMe), 1.23 (s, 9H);  $^{13}C$  NMR  $\delta$  200.3 (CO), 160.9 (d,  $J = 2$  Hz, C-OMe), 135.4 (d,  $J = 9$  Hz, Ar CH), 133.9 (d,  $J = 2$  Hz, Ar CH), 131.0 (d,  $J = 3$  Hz, Ph C-4), 130.8 (d,  $J = 10$  Hz, 2CH, Ph C-2), 129.4 (d,  $J = 89$  Hz, C, Ph C-1), 128.4 (d,  $J = 12$  Hz, 2CH, Ph C-3), 121.5 (d,  $J = 12$  Hz, Ar CH), 115.2 (d,  $J = 86$  Hz, C, Ar C-1), 111.5 (d,  $J = 6$  Hz, Ar CH), 55.3 (OMe), 47.7 (d,  $J = 109$  Hz, P=C), 40.5 (d,  $J = 12$  Hz,  $CMe_3$ ), 28.8 ( $CMe_3$ ), 11.3 (d,  $J = 65$  Hz, PMe);  $^{31}P$  NMR  $\delta$  +9.4; MS (ES)  $m/z$  329 ( $M^++H$ , 100); HRMS: Calcd for  $C_{20}H_{26}O_2P$  ( $M+H$ ): 329.1670. Found: 329.1672; Anal. Calcd for  $C_{20}H_{25}O_2P$ : C, 73.15; H, 7.67. Found: 72.87; H, 7.23.

### Preparation of 1-((2-chlorophenyl)methyl(phenyl)phosphoranylidene)-3,3-dimethylbutan-2-one **26**

The same method as for **25** using (2-chlorophenyl)methylphenylphosphine **22** (1.33 g, 5.7 mmol) and 1-bromo-3,3-dimethylbutan-2-one **24** (1.02 g, 5.7 mmol) gave the product **26** (0.32 g, 17%) as pale yellow crystals; mp 104–106 °C;  $^1H$  NMR  $\delta$  7.90–7.84 (m, 1H), 7.56–7.51 (m, 3H), 7.48–7.40 (m, 5H), 3.44 (d,  $J = 27$  Hz, P=CH), 2.52 (d,  $J = 14$  Hz, PMe), 1.19 (s, 9H);  $^{13}C$  NMR  $\delta$  200.7 (CO), 136.6 (d,  $J = 4$  Hz, C-Cl), 136.4 (d,  $J = 11$  Hz, Ar CH), 133.3 (d,  $J = 3$  Hz, Ph C-4), 131.6 (d,  $J = 3$  Hz, Ar CH), 131.02 (d,  $J = 10$  Hz, 2CH, Ph C-2), 130.95 (d,  $J = 5$  Hz, Ar CH), 128.8 (d,  $J = 12$  Hz, 2CH, Ph C-3), 127.9 (d,  $J$

= 90 Hz, C, Ph C-1), 127.2 (d,  $J = 12$  Hz, Ar CH), 126.0 (d,  $J = 85$  Hz, C, Ar C-1), 48.8 (d,  $J = 110$  Hz, P=CH), 40.5 (d,  $J = 12$  Hz,  $CMe_3$ ), 28.7 ( $CMe_3$ ), 11.2 (d,  $J = 65$  Hz, PMe);  $^{31}P$  NMR  $\delta +12.0$ ; MS (CI)  $m/z$  335 ( $^{37}Cl$ -M+H, 20), 333 ( $^{35}Cl$ -M+H, 100), 277 (14), 275 (56), 253 (5), 251 (18); HRMS (CI): Calcd for  $C_{19}H_{23}ClOP$  (M+H): 333.1175. Found: 333.1180.

#### Preparation of 1-((2-methylphenyl)methyl(phenyl)phosphoranylidene)-3,3-dimethylbutan-2-one **27**

The same method as for **25** using (2-methylphenyl)methylphenylphosphine **23** (1.88 g, 8.9 mmol) and 1-bromo-3,3-dimethylbutan-2-one **24** (1.58 g, 8.9 mmol), with recrystallisation from EtOAc gave the product **27** (0.71 g, 26%) as colourless crystals; mp 116–117 °C ;  $^1H$  NMR  $\delta$  7.61–7.49 (m, 4H), 7.47–7.41 (m, 3H), 7.31–7.27 (m, 1H), 7.25–7.22 (m, 1H), 3.50 (d,  $J = 27$  Hz, 1H, P=CH), 2.40 (d,  $J = 16$  Hz, 3H, PMe), 2.29 (s, 3H, Ar-Me), 1.19 (s, 9H);  $^{13}C$  NMR  $\delta$  200.2 (CO), 141.4 (d,  $J = 8$  Hz, Ar CMe), 133.1 (d,  $J = 11$  Hz, Ar CH), 132.1 (d,  $J = 10$  Hz, Ar CH), 132.0 (d,  $J = 3$  Hz, Ph C-4), 131.6 (d,  $J = 3$  Hz, Ar CH), 131.3 (d,  $J = 11$  Hz, 2CH, Ph C-2), 128.9 (d,  $J = 12$  Hz, 2CH, Ph C-3), 126.1 (d,  $J = 13$  Hz, Ar CH), 28.6 ( $CMe_3$ ), 21.7 (d,  $J = 5$  Hz, Ar-Me), 12.4 (d,  $J = 68$  Hz, PMe) [signals for Ph C-1, Ar C-1, P=CH and  $CMe_3$  not apparent];  $^{31}P$  NMR  $\delta +9.3$ ; MS (ES)  $m/z$  313 ( $M^+$ +H, 100); MS (EI)  $m/z$  312 ( $M^+$ , 3), 255 ( $M-Bu^+$ , 100); HRMS (EI): Calcd for  $C_{20}H_{25}OP$  ( $M^+$ ): 312.1643. Found: 312.1645.

#### Preparation of 1-((2-methoxyphenyl)methyl(phenyl)phosphoranylidene)-3,3-dimethylbutane-2-thione **28**

A solution of ylide **25** (1.0 g, 3 mmol) in dry  $CH_2Cl_2$  (40 mL) was stirred at rt under nitrogen while trifluoromethanesulfonic anhydride (0.86 g, 0.50 mL, 3 mmol) was added dropwise. After the addition the mixture was stirred for 1 h and then evaporated under reduced pressure and the residue was taken up in dry DMF (30 mL). Anhydrous sodium sulfide (0.35 g, 4.5 mmol) was added and the mixture was stirred at rt for 72 h. The mixture was then added to water (100 mL) and the product was extracted with diethyl ether (3  $\times$  20 mL). The extracts were washed thoroughly with water, dried and evaporated to give the product **28** (0.22 g, 21%) as a brown oil;  $^1H$  NMR  $\delta$  7.62–7.59 (m, 1H), 7.57–7.42 (m, 6H), 7.07–7.01 (m, 1H), 7.00–6.94 (m, 1H), 4.89 (d,  $J = 33$  Hz, P=CH), 3.70 (s, 3H, OMe), 2.78 (d,  $J = 15$  Hz, 3H, PMe), 1.37 (s, 9H);  $^{13}C$  NMR  $\delta$  211.2 (d,  $J = 3$  Hz, CS), 160.9 (d,  $J = 2$  Hz, C-OMe), 135.5 (d,  $J = 8$  Hz, Ar CH), 134.2 (d,  $J = 2$  Hz, Ar CH), 131.4 (d,  $J = 3$  Hz, Ph C-4), 130.8 (d,  $J = 9$  Hz, 2CH, Ph C-2), 128.6 (d,  $J = 12$  Hz, 2CH, Ph C-3), 127.2 (d,  $J = 89$  Hz, C, Ph C-1), 121.0 (d,  $J = 12$  Hz, Ar CH), 112.0 (d,  $J = 90$  Hz, C, Ar C-1), 111.5 (d,  $J = 6$  Hz, Ar CH), 83.8 (d,  $J = 115$  Hz, P=C), 55.3 (OMe), 43.1 (d,  $J = 14$  Hz,  $CMe_3$ ), 28.0 ( $CMe_3$ ), 10.7 (d,  $J = 67$  Hz, PMe);  $^{31}P$  NMR  $\delta +1.2$ .

#### Preparation of 1-((2-chlorophenyl)methyl(phenyl)phosphoranylidene)-3,3-dimethylbutane-2-thione **29**

The same method as for **28** using ylide **26** (0.15 g, 0.45 mmol), trifluoromethanesulfonic anhydride (0.17 g, 0.62 mmol) and sodium sulfide (0.35 g, 4.5 mmol) gave the product **29** (0.09 g, 60%) as an orange oil;

$^1\text{H}$  NMR  $\delta$  7.90–7.82 (m, 1H), 7.57–7.34 (m, 8H), 4.90 (d,  $J$  = 35 Hz, P=CH), 2.51 (d,  $J$  = 14 Hz, 3H, PMe), 1.36 (s, 9H);  $^{31}\text{P}$  NMR  $\delta$  +0.9.

### Preparation of 1-((2-methylphenyl)methyl(phenyl)phosphoranylidene)-3,3-dimethylbutane-2-thione **30**

The same method as for **28** using ylide **27** (0.22 g, 0.78 mmol), trifluoromethanesulfonic anhydride (0.24 g, 0.78 mmol) and sodium sulfide (90 mg, 1.15 mmol) gave the product **30** (0.12 g, 48%) as a yellow oil;  $^1\text{H}$  NMR  $\delta$  7.62–7.38 (m, 7H), 7.31–7.17 (m, 2H), 4.99 (d,  $J$  = 34 Hz, P=CH), 2.76 (d,  $J$  = 14 Hz, 3H, PMe), 2.35 (s, 3H, Ar-Me), 1.37 (s, 9H);  $^{13}\text{C}$  NMR  $\delta$  211.7 (d,  $J$  = 4 Hz, CS), 140.8 (d,  $J$  = 8 Hz, Ar CMe), 133.8 (d,  $J$  = 10 Hz, Ar CH), 132.8 (d,  $J$  = 11 Hz, Ar CH), 132.0 (d,  $J$  = Hz, Ph C-4), 131.8 (d,  $J$  = 11 Hz, Ar CH), 131.2 (d,  $J$  = 9 Hz, 2CH, Ph C-2), 131.1 (d,  $J$  = 10 Hz, Ar CH), 128.7 (d,  $J$  = 12 Hz, 2CH, Ph C-3), 126.7 (d,  $J$  = 86 Hz, Ph C-1), 125.8 (d,  $J$  = 7 Hz, Ar CH), 123.9 (d,  $J$  = 88 Hz, Ar C-1), 83.5 (d,  $J$  = 114 Hz, P=CH), 43.1 (d,  $J$  = 14 Hz, CMe<sub>3</sub>), 28.5 (CMe<sub>3</sub>), 21.5 (d,  $J$  = 5 Hz, Ar-Me), 12.5 (d,  $J$  = 67 Hz, PMe);  $^{31}\text{P}$  NMR  $\delta$  +1.2; HRMS (CI): Calcd for C<sub>20</sub>H<sub>26</sub>PS (M+H): 329.1493. Found: 329.1498.

### Pyrolysis of ylide **28** leading to formation an involatile residue of 2-tert-butyl-4-methyl-4-phenyl-1,4-benzoxaphosphinium salt **34**

A sample of ylide **28** (170 mg) was subjected to FVP at 550 C and 10<sup>-2</sup> Torr. Analysis of the residual solid left in the inlet tube showed it to consist mainly of the salt **34** (30 mg);  $^1\text{H}$  NMR  $\delta$  7.98–7.87 (m, 3H), 7.79–7.74 (m, 1H), 7.68–7.56 (m, 3H), 7.51–7.46 (m, 1H), 7.42–7.37 (m, 1H), 6.16 (d,  $J$  = 8 Hz, =CH–), 2.87 (d,  $J$  = 14 Hz, PMe), 1.38 (s, 9H);  $^{13}\text{C}$  NMR  $\delta$  178.4 (d,  $J$  = 4.5, C-2), 155.0 (d,  $J$  = 2 Hz, C-8a), 136.1 (d,  $J$  = 2 Hz, CH, Ph C-4), 134.3 (d,  $J$  = 3 Hz, CH, C-5), 132.1 (d,  $J$  = 12 Hz, 2CH, Ph C-2), 131.6 (d,  $J$  = 7 Hz, CH, C-7), 130.0 (d,  $J$  = 14 Hz, 2CH, Ph C-3), 127.1 (d,  $J$  = 12 Hz, CH, C-6), 123.7 (d,  $J$  = 93 Hz, Ph C-1), 119.1 (d,  $J$  = 5 Hz, CH, C-8), 100.9 (d,  $J$  = 89 Hz, C-4a), 74.9 (d,  $J$  = 89 Hz, CH, C-3), 39.1 (d,  $J$  = 9 Hz, CMe<sub>3</sub>), 27.7 (CMe<sub>3</sub>), 12.9 (d,  $J$  = 61 Hz, PMe);  $^{31}\text{P}$  NMR  $\delta$  –10.2; HRMS (ES) Calcd for C<sub>19</sub>H<sub>22</sub>OP (M<sup>+</sup>): 297.1408. Found: 297.1401.

### Pyrolysis of ylide **26** leading to formation of an involatile residue of 2-tert-butyl-4-methyl-4-phenyl-1,4-benzoxaphosphinium chloride **34**

A sample of ylide **26** (40 mg) was subjected to FVP at 550 C and 10<sup>-2</sup> Torr. Analysis of the residual solid left in the inlet tube showed it to consist mainly of the chloride salt **34** (10 mg);  $^1\text{H}$  NMR  $\delta$  8.2–7.4 (m, 9H), 6.34 (d,  $J$  = 8 Hz, =CH–), 3.11 (d,  $J$  = 15 Hz, PMe), 1.39 (s, 9H);  $^{13}\text{C}$  NMR  $\delta$  136.1 (d,  $J$  = 2 Hz, CH, Ph C-4), 134.3 (d,  $J$  = 3 Hz, CH, C-5), 132.2 (d,  $J$  = 12 Hz, 2CH, Ph C-2), 131.7 (d,  $J$  = 7 Hz, CH, C-7), 130.0 (d,  $J$  = 14 Hz, 2CH, Ph C-3), 127.2 (d,  $J$  = 11 Hz, CH, C-6), 123.7 (d,  $J$  = 93 Hz, Ph C-1), 119.1 (d,  $J$  = 5 Hz, CH, C-8), 100.9 (d,  $J$  = 89 Hz, C-4a), 74.9 (d,  $J$  = 89 Hz, CH, C-3), 39.1 (CMe<sub>3</sub>), 27.7 (CMe<sub>3</sub>), 13.0 (d,  $J$  = 61 Hz, PMe) [C-2 and C-8a not apparent];  $^{31}\text{P}$  NMR  $\delta$  –10.4; HRMS (ES) Calcd for C<sub>19</sub>H<sub>22</sub>OP (M<sup>+</sup>): 297.1408. Found: 297.1413.

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