Novel Quasiphosphonium Ylides from the Reaction of Trialkyl Phosphites with Dialkyl Benzoylphosphonates: Evidence for Carbene Intermediates in the Intramolecular Cyclisation of 2-Substituted Dialkyl Benzoylphosphonates

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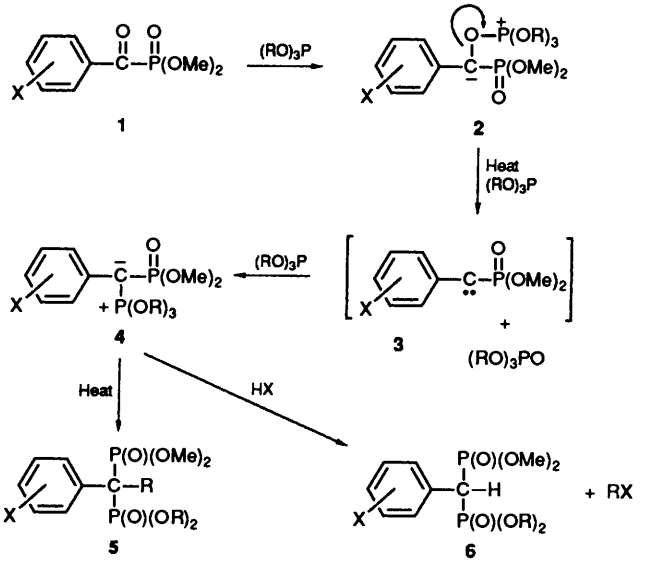
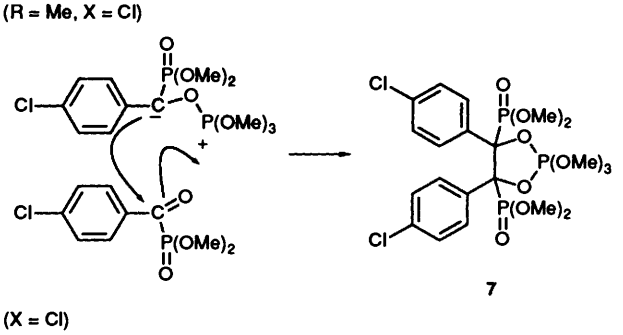
The reaction of dialkyl aroylphosphonates **1** with trialkyl phosphites leads to the formation of novel quasiphosphonium ylides **4** which in some cases thermally rearrange to the bisphosphonates **5**. 2-Substituted dialkyl aroylphosphonates may also undergo intramolecular cyclisation under these conditions. Evidence is presented for the involvement of the carbene intermediates **3**.

We have previously shown that the reaction of trialkyl phosphites with dialkyl benzoylphosphonates **1** in the presence of electrophiles involves an initial attack by the phosphite on the carbonyl oxygen of the aroylphosphonate to give anionic intermediates **2** which then react with the electrophile.[1,2] We have now shown that under appropriate conditions trialkyl phosphites will also react with dialkyl aroylphosphonates in the absence of electrophiles and that such reactions proceed *via* carbene intermediates **3**.[3]

At room temperature the reaction between trialkyl phosphites and dialkyl benzoylphosphonates usually only proceed at a significant rate if an electrophile is present to trap the anionic intermediate as it forms. However, at higher temperatures we have found that trialkyl phosphites react with dialkyl benzoylphosphonates to give novel ylidic phosphonates **4** which, in some cases, rearrange to give bisphosphonates **5**.



Thus, for example, dimethyl 4-methoxybenzoylphosphonate **1** (X = 4-OMe) when heated with trimethyl phosphite for 4 h at 105 °C gave equimolar amounts of the bisphosphonates **5** (R = Me, X = 4-OMe) and trimethyl phosphate. By monitoring the course of this reactions by NMR spectroscopy it was possible to identify the precursor of this bisphosphonate as the novel quasiphosphonium ylide **4** (R = Me, X = 4-OMe) giving two doublets in the ^{31}P NMR spectrum at δ_P 30.7 and 53.9 (J_{PP}/Hz 95). The doublet at δ_P 30.7 was shown to be derived from the benzoylphosphonate **1** (X = 4-OMe) while that at δ_P 53.9 was shown to be derived from trimethyl phosphite. ^{13}C NMR spectroscopy confirmed that both phosphorus atoms were attached to the same quaternary carbon [δ_C 27.5 (dd, $^1J_{PC}$/Hz 211 and 224]. Similar behaviour was observed for the dimethyl benzoylphosphonates **1** (X = H, 4-Me, and 4-Cl), although at lower temperatures a competing side reaction was observed for the case of the chloro-substituted system **1** (X = 4-Cl) leading to the formation of the 1,3,2-dioxaphospholane **7**. This arises because of the enhanced ability



Scheme 1

of the dimethyl 4-chlorobenzoylphosphonate to function as an electrophile and to intercept the initially formed anionic intermediate **2** (R = Me, X = Cl) (Scheme 1). Attempts to purify the 1,3,2-dioxaphospholane **7** by distillation led to its decomposition and the regeneration of the trimethyl phosphite and dimethyl 4-chlorobenzoylphosphonate. This latter behaviour may, in part, explain why the preparation of the bisphosphonate **5** (R = Me, X = 4-Cl) can be achieved without significant formation of the 1,3,2-dioxaphospholane **7** at 105 °C.

Interestingly, the more electrophilic dichloro-substituted benzoylphosphonate **1** (X = 2,4-Cl_2) showed no tendency, even at room temperature, to form a 1,3,2-dioxaphospholane analogous to **7**, although the formation of the ylidic phosphonate **4** (R = Me, X = 2,4-Cl_2) was observed over a period of several days. Thus, while steric hindrance by the *ortho*-chloro group in the anionic intermediate **2** (R = Me, X = 2,4-Cl_2) appears to inhibit reaction with further benzoylphosphonate **1** (X = 2,4-Cl_2) decomposition of the anionic intermediate **2**

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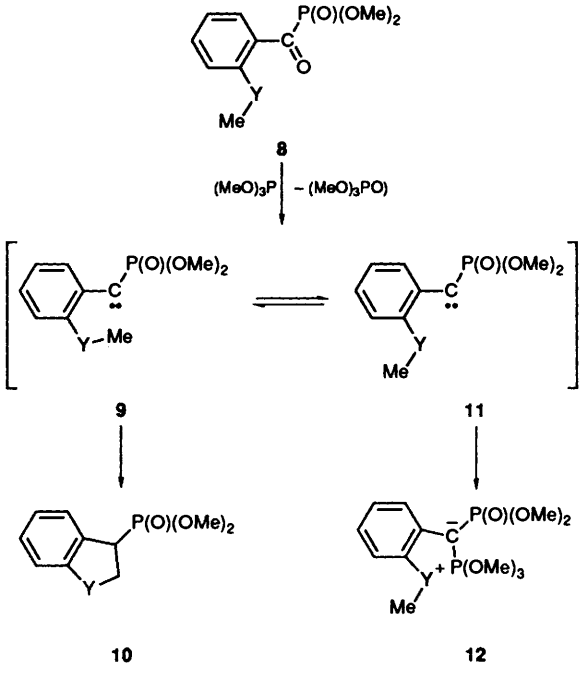
(R = Me, X = 2,4-Cl_2) to give the carbene intermediate **3** (R = Me, X = 2,4-Cl_2) proceeds normally to give the observed ylidic phosphonate **4** (R = Me, X = 2,4-Cl_2).

While the trismethoxyphosphonium ylides **4** (R = Me) tended to rearrange to the corresponding bisphosphonates **5** (R = Me) under the conditions needed for their formation, the corresponding trisethoxyphosphonium ylides **4** (R = Et) were much more resistant to thermal rearrangement. Thus, for example, it was possible to prepare the trisethoxyphosphonium ylide **4** (R = Et, X = 4-OMe) in essentially quantitative yield by simply heating dimethyl 4-methoxybenzoylphosphonate **1** (X = 4-OMe) with triethyl phosphite for 10 h at 85 °C.

The formation of the ylidic phosphonates **4** is readily explained if it is proposed that the initially formed anionic intermediates **2** undergo cleavage of the α-C–O bond to give carbenes **3**, since trivalent phosphorus compounds are known to be efficient traps for carbenes leading to ylide formation.[4] The involvement of carbene intermediates has been suspected in a number of reactions involving the deoxygenation of carbonyl groups by trivalent phosphorus compounds but in the past it has been difficult to obtain conclusive evidence to support such a mechanism.[5a]

To obtain conclusive evidence for the involvement of the carbene intermediates **3**, carbene traps were added to the reaction mixture. However, because trialkyl phosphites are themselves very efficient carbene traps we were unable to compete successfully with the formation of the ylides **4** using

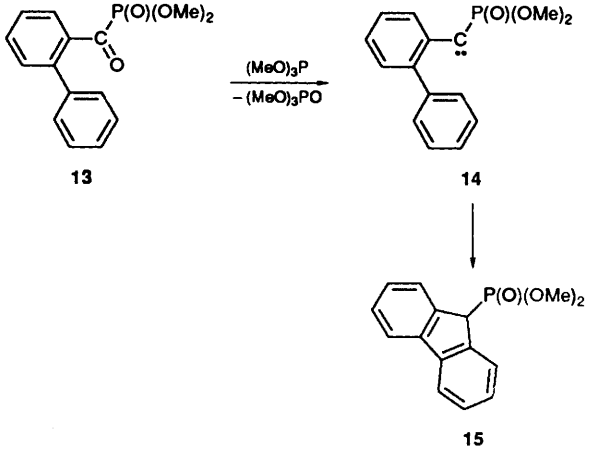


the usual trapping agents, such as cyclohexene. We therefore investigated using a substituted benzoylphosphonate where the substituent could react rapidly by an intramolecular route with any carbene intermediate formed. Dimethyl 2-ethylbenzoylphosphonate **8** (Y = CH_2) was chosen since any subsequent intramolecular cyclisation of the proposed carbene intermediate **9** (Y = CH_2), by insertion into the terminal C–H bond of the ethyl group, would be difficult to explain other than by the involvement of a carbene intermediate.

Dimethyl 2-ethylbenzoylphosphonate **8** (Y = CH_2) when heated with trimethyl phosphite at 105 °C for 3 h gave two major products in addition to trimethyl phosphate. These were subsequently identified as the ylidic phosphonate **12** (Y = CH_2) and the indan-1-ylphosphonate **10** (Y = CH_2), the latter being formed by an intramolecular cyclisation *via* the proposed carbene intermediate **9** (Y = CH_2). The cyclisation of the benzoylphosphonate **8** (Y = CH_2) to the indan-1-ylphosphonate **10** (Y = CH_2) was clearly shown in the ^1H and ^{13}C NMR spectra of the product by the loss of the signals corresponding to the ethyl substituent and the appearance of signals associated with the presence of a CH group adjacent to the phosphonate group. We believe that this cyclisation is conclusive evidence for the involvement of a carbene intermediate in this reaction. This also strongly suggests that the reported cyclisation of some other *ortho*-substituted benzoylphosphonates[6] proceed *via* a carbene mechanism rather than the unsatisfactory anionic mechanism proposed. The high proportion of the ylidic phosphonate **12** (Y = CH_2) formed in this reaction again provides evidence for the high efficiency of the trimethyl phosphite in trapping the carbene intermediate (**9** ⇌ **11**; Y = CH_2) *via* an intermolecular mechanism in direct competition with the intramolecular route leading to cyclisation. Interestingly, the ylidic phosphonate **12** (Y = CH_2) showed little tendency to rearrange to the corresponding bisphosphonate **5** (R = Me, X = 2-Et), as had been observed with the 4-substituted benzoylphosphonates previously discussed. We must conclude that the thermal rearrangement of the ylidic phosphonate **12** (Y = CH_2) is inhibited by steric factors since similar behaviour has been observed with other 2-substituted benzoylphosphonates we have studied. The ylidic phosphonate **12** (Y = CH_2) was isolated as its decomposition product, the bisphosphonate **6** (R = Me, X = 2-Et), when attempts were made to isolate it by chromatography.

In the case of the 2-methoxy substituted benzoylphosphonate **8** (Y = O), it was found that the ratio of cyclisation to ylide formation was very sensitive to the reaction temperature. Thus, for example, when the benzoylphosphonate **8** (X = O) was heated with 3 mol equiv. of trimethyl phosphite at 105 °C the ratio of cyclisation to ylide formation was 3:1, whereas at 20 °C the ratio became 1:4. This could be explained by proposing that the conformation necessary for intramolecular carbene insertion **9** is only significantly populated at the higher temperatures, and that at lower temperatures the conformation **11** is favoured facilitating attack by the trimethyl phosphite leading to ylide formation.

Alternatively, the lack of cyclisation at lower temperatures could be interpreted as indicating that ylide formation occurs *via* a non-carbenoid mechanism and that carbene intermediates are only formed in significant quantities at higher temperatures. To investigate this latter possibility we examined the reaction of dimethyl 2-phenylbenzoylphosphonate 13 with trimethyl



phosphite. Conjugation between the two benzene rings in this phosphonate should stabilise the coplanar conformation of the proposed carbene intermediate **14** thus favouring an intra-

molecular reaction pathway even at room temperature. After only *ca.* 40 min at 90 °C the reaction of the 2-phenylbenzoylphosphonate **13** with trimethyl phosphite was complete and the expected cyclisation product **15** was present in high yield. There was no sign of the ylidic phosphonate **4** (R = Me, X = 2-Ph) in the ^{31}P NMR spectrum of the reaction mixture. This reaction was also repeated at room temperature, and although under these conditions the reaction was considerably slower, taking some 10 days, the cyclisation product **15** was again the only major product with no sign of the ylidic phosphonate **4** (R = Me, X = 2-Ph). In contrast, the reaction of the corresponding 4-phenyl substituted benzoylphosphonate **1** (X = 4-Ph) with trimethyl phosphite, where intramolecular carbene insertion is prevented, led to reaction only *via* the ylidic phosphonate **4** (R = Me, X = 4-Ph) [$\delta_P(CDCl_3)$ 30.7 and 55.3 (J_{PP}/Hz 88]. Because of these observations and, in particular, the formation of the cyclisation product **15** at room temperatures we may, therefore, conclude that carbene formation can occur even at these lower temperatures. The change in the product ratio in the case of the 2-methoxy substituted system **8** (Y = O) would, therefore, appear to be due to conformational factors.

As expected, the product ratio in the 2-methoxy-substituted system **8** (Y = O) can also be dramatically affected by the addition of an inert solvent to the reaction mixture. Under these circumstances the intermolecular process leading to ylide formation can be effectively suppressed in favour of intramolecular cyclisation.

The synthetic potential of these carbene insertions is currently being assessed. The analogous deoxygenation of nitro groups by trivalent phosphorus compounds, such as trialkyl phosphites, to give nitrenes is well established[5b] and has been shown to offer substantial synthetic potential.

Experimental

NMR spectra were determined on either JEOL FX100 or GSX270 spectrometers; *J* values are recorded in Hz.

Preparation of Dimethyl Benzoylphosphonates.—The dimethyl benzoylphosphonates were prepared in high yield by the addition of the appropriate benzoyl chloride to an equimolar quantity of trimethyl phosphite in dry toluene. Where the benzoyl chlorides were not readily available they were prepared by the action of thionyl chloride on the corresponding benzoic acid. All thionyl chloride must be removed from the benzoyl chloride before its addition to the trimethyl phosphite.

Dimethyl benzoylphosphonate **1** (X = H). This compound was obtained as a pale yellow oil (41.8 g, 97%), b.p. 102 °C at 0.03 mmHg (lit.,[7] b.p. 146 °C at 2.5 mmHg) (Found: C, 50.2; H, 5.25. Calc. for $C_9H_{11}O_4P$: C, 50.47; H, 5.18%); $\delta_P(CDCl_3)$ 0.6; $\delta_C(CDCl_3)$ 53.7 (d, J_{PC} 7, MeOP), 128.4 (C-3, C-5), 129.2 (d, J_{PC} 2, C-2, C-6), 134.5 (C-4), 134.9 (d, J_{PC} 64, C-1), 197.8 (d, J_{PC} 174, C=O); δ_H(100 MHz; $CDCl_3$) 3.93 (6 H, d, J_{PH} 11, MeOP), 7.40–7.71 (3 H, m, 3-H, 4-H, 5-H) and 8.19–8.36 (2 H, m, 2-H, 6-H).

Dimethyl 4-methylbenzoylphosphonate **1** (X = 4-Me). This compound was obtained as a pale yellow oil (41.5 g, 91%), b.p. 110 °C at 0.035 mmHg (lit.,[8] b.p. 130–134 °C at *ca.* 760 mmHg) (Found: C, 52.6; H, 5.65. Calc. for $C_{10}H_{13}O_4P$: C, 52.64; H, 5.74%); $\delta_P(CDCl_3)$ 0.9; $\delta_C(CDCl_3)$ 21.2 (Me), 53.5 (d, J_{PC} 7, MeOP), 129.0 (C-3, C-5), 129.3 (d, J_{PC} 2, C-2, C-6), 132.6 (d, J_{PC} 65, C-1), 145.7 (C-4) and 196.8 (d, J_{PC} 174, C=O); δ_H(100 MHz; $CDCl_3$) 2.43 (3 H, s, Me), 3.92 (6 H, d, J_{PH} 11, MeOP), 7.31 (2 H, br d, J_{HH} 8, 2-H, 6-H) and 8.16 (2 H, d, J_{HH} 8, 3-H, 5-H).

Dimethyl 4-methoxybenzoylphosphonate **1** (X = 4-MeO). This compound was obtained as a pale yellow oil (45.5 g, 93%), b.p. 125 °C at 0.03 mmHg (lit.,[7] b.p. 170 °C at 2.5 mmHg) (Found: C, 49.45; H, 5.6. Calc. for $C_{10}H_{13}O_5P$: C, 49.19; H, 5.37%); $\delta_P(CDCl_3)$ 1.4; $\delta_C(CDCl_3)$ 53.5 (d, J_{PC} 7, MeOP), 55.1 (MeO), 113.7 (C-3, C-5), 128.3 (d, J_{PC} 66, C-1), 131.9 (d, J_{PC} 2, C-2, C.6), 164.6 (C-4) and 195.2 (d, J_{PC} 173, C=O); δ_H(100 MHz; $CDCl_3$) 3.90 (3 H, s, MeO), 3.91 (6 H, d, J_{PH} 11, MeOP), 6.98 (2 H, dd, J_{HH} 9, J_{PH} 1, 3-H, 5-H) and 8.27 (2 H, d, J_{HH} 9, 2-H, 6-H).

Dimethyl 4-chlorobenzoylphosphonate **1** (X = 4-Cl). This compound was obtained as a pale yellow oil (45.5 g, 92%), b.p. 114 °C at 0.04 mmHg (lit.,[7] b.p. 136 °C at 1.5 mmHg) (Found: C, 43.65; H, 4.1. Calc. for $C_9H_{10}ClO_4P$: C, 43.48; H, 4.05%); $\delta_P(CDCl_3)$ 0.3; $\delta_C(CDCl_3)$ 53.5 (d, J_{PC} 7, MeOP), 128.5 (C-3, C-5), 130.4 (d, J_{PC} 2, C-2, C-6), 133.1 (d, J_{PC} 65, C-1), 140.7 (C-4) and 196.3 (d, J_{PC} 177, C=O); δ_H(100 MHz; $CDCl_3$) 3.93 (6 H, d, J_{PH} 11, MeOP), 7.50 (2 H, br d, J_{HH} 9, 3-H, 5-H) and 8.23 (2 H, d, J_{HH} 9, 2-H, 6-H).

Dimethyl 4-phenylbenzoylphosphonate **1** (X = Ph). This compound was obtained as a colourless oil (10.4 g, 78%), b.p. 181 °C at 0.15 mmHg (Found: C, 61.75; H, 5.1. Calc. for $C_{15}H_{15}O_4P$: C, 62.07; H, 5.21%); $\delta_P(CDCl_3)$ 1.4; $\delta_C(CDCl_3)$ 53.5 (d, J_{PC} 7, MeOP), 126.6 (C-2′, C-6′), 126.8 (C-3, C-5), 128.0 (C-4′), 128.4 (C-3′, C-5′), 129.8 (d, J_{PC} 2, C-2, C-6), 133.6 (d, J_{PC} 64, C-1), 138.6 (C-1′), 146.7 (C-4) and 197.1 (d, J_{PC} 175, C=O); δ_H(270 MHz; $CDCl_3$) 3.94 (6 H, d, J_{PH} 11, MeOP), 7.36–7.49 (3 H, m, 3′-H, 4′-H, 5′-H), 7.61 (2 H, m, 2′-H, 6′-H), 7.72 (2 H, br d, *J* 8, 3-H, 5-H) and 8.33 (2 H, d, *J* 8, 2-H, 6-H).

Dimethyl 2,4-dichlorobenzoylphosphonate **1** (X = 2,4-diCl). This compound was obtained as a pale yellow oil (4.3 g, 58%), b.p. 136 °C at 0.2 mmHg (Found: C, 37.95; H, 3.15. $C_9H_9Cl_2O_4P$ requires C, 38.19; H, 3.2%); $\delta_P(CDCl_3)$ −1.0; $\delta_C(CDCl_3)$ 53.8 (d, J_{PC} 7, MeOP), 126.6 (C-5), 130.7 (d, J_{PC} 3, C-3), 132.3 (d, J_{PC} C-6), 132.5 (d, J_{PC} 66, C-1), 132.9 (d, J_{PC} 6, C-2), 138.9 (C-4) and 197.7 (d, J_{PC} 184, C=O); δ_H(270 MHz; $CDCl_3$) 3.92 (6 H, d, J_{PH} 11, MeOP), 7.40 (1 H, dd, J_{HH} 9 and 2, 3-H, 6-H), 7.51 (1 H, t, J_{PH} 2, J_{HH} 2, 3-H) and 8.21 (1 H, d, J_{HH} 9, 5-H).

Dimethyl 2-methoxybenzoylphosphonate **8** (Y = O). This compound was obtained as a colourless oil (7.8 g, 80%), b.p. 154°C at 0.03 mmHg (lit.,[8] b.p. 165–170 °C at *ca.* 760 mmHg), M^+, 244 (Found: C, 49.2; H, 5.3. Calc. for $C_{10}H_{13}O_5P$: C, 49.19; H, 5.37%); $\delta_P(CDCl_3)$ 0.7; $\delta_C(CDCl_3)$ 53.65 (d, J_{PC} 7, MeOP), 55.56 (MeO), 111.8 (C-3), 120.3 (C-5), 126.1 (d, J_{PC} 63, C-1), 130.5 (d, J_{PC} 2, C-6), 135.2 (C-4), 159.2 (d, J_{PC} 2, C-2), and 199.0 (d, J_{PC} 180, C=O); δ_H(270 MHz; $CDCl_3$) 3.89 (6 H, d, J_{PH}, MeOP), 3.94 (3 H, s, MeO), 7.00–7.07 (2 H, m, 3-H, 5-H), 7.56 (1 H, ddd, *J* 2, 7.5 and 8, 4-H) and 7.88 (1 H, dd, *J* 2 and 8, 6-H).

Dimethyl 2-phenylbenzoylphosphonate **13**. This compound was obtained as a colourless oil (13.2 g, 73%), b.p. 178 °C at 0.005 mmHg, M^+, 290 (Found: C, 62.0; H, 4.95. Calc. for $C_{15}H_{15}O_4P$: C, 62.07; H, 5.21%); $\delta_P(CDCl_3)$ −0.8; $\delta_C(CDCl_3)$ 53.7 (d, J_{PC} 7, MeO), 127.0 (C-5), 127.2 (C-4′), 128.0 (C-3′, C-5′), 128.6 (C-2′, C-6′), 129.3 (C-6), 130.9 (d, J_{PC} 2, C-3), 132.1 (C-4), 136.6 (d, J_{PC} 63, C-1), 139.6 (C-1′), 141.7 (d, J_{PC} 5, C-2) and 202.9 (d, J_{PC} 176, C=O); δ_H(270 MHz; $CDCl_3$) 3.75 (6 H, d, J_{PH} 11, MeOP), 7.25–7.30 (2 H, m, 2′-H, 6′-H), 7.34–7.42 (4 H, m, 3-H, 3′-H, 4′-H, 5′-H), 7.46 (1 H, td, *J* 1 and 8, 5-H), 7.57 (1 H, td, *J* 1 and 8, 4-H) and 8.09 (1 H, dd, *J* 1 and 8, 6-H).

Reactions of Dimethyl Benzoylphosphonates with Trimethyl Phosphite.—*Tetramethyl 1-phenylethane-1,1-diphosphonate* **5** (R = Me, X = H). A stirred mixture of dimethyl benzoylphosphonate (3 g, 14 mmol) and trimethyl phosphite (7 g, 56 mmol) was heated under dry nitrogen at 105 °C. ^{31}P NMR spectroscopy initially showed the formation of equimolar quantities of trimethyl phosphate and the ylide [*(dimethoxyphosphinyl)(phenyl)methylene]trismethoxyphosphorane* **4** (R = Me, X = H), $\delta_P(CDCl_3)$ 31.0 [d, J_{PP} 89, P(O)(OMe)$_2$] and

54.5 [d, J_{PP} 89, $P(OMe)_3$]; $\delta_C(CDCl_3)$ 29.7 (dd, J_{PC} 209 and 222, αC). However, as the reaction proceeded the ylide **4** (R = Me, X = H) was observed to rearrange to the bisphosphonate (R = Me, X = H). After 4 h formation of the bisphosphonate was complete. The resulting yellow solution was then heated at 60 °C under reduced pressure (0.05 mmHg) to remove the excess of trimethyl phosphite and other volatile components. The residue, which crystallized on cooling, was washed with diethyl ether and then dried *in vacuo*. The product (2.6 g, 58%) was isolated as a white solid, b.p. 140 °C at 0.05 mmHg, containing a small quantity of the bisphosphonate, *tetramethyl phenylmethanediphosphonate* **6** (R = Me, X = H). An analytically pure sample of the bisphosphonate **5** (R = Me, X = H) was isolated by reverse phase HPLC using methanol–water (60:40) as eluent, m.p. 120 °C, M^+, 322 (Found: C, 44.8; H, 6.15; $C_{12}H_{20}O_6P_2$ requires C, 44.73; H, 6.26%); $\delta_P(CDCl_3)$ 25.0; $\delta_C(CDCl_3)$ 17.1 (t, J_{PC} 7, Me), 46.4 (t, J_{PC} 132, αC), 53.8 (t, J_{PC} 3, MeOP), 54.1 (t, J_{PC} 3, MeOP), 127.4 (t, J_{PC} 2, C-4), 127.9 (t, J_{PC} 2, C-3, C-5), 128.6 (t, J_{PC} 6, C-2, C-6) and 133.2 (t, J_{PC} 7, C-1); δ_H(100 MHz; $CDCl_3$) 1.95 (3 H, t, J_{PH} 6, Me), 3.61 (3 H, d, J_{PH} 11, MeOP), 3.73 (3 H, d, J_{PH} 11, MeOP), 7.23–7.50 (3 H, m, 3-H, 4-H, 5-H) and 7.68–7.90 (2 H, m, 2-H, 6-H).

Tetramethyl 1-(4-*methylphenyl*)*ethane*-1,1-*diphosphonate* **5** (R = Me, X = 4-Me). A stirred mixture of dimethyl 4-methylbenzoylphosphonate (3.2 g, 14 mmol) and trimethyl phosphite (7 g, 56 mmol) was heated under dry nitrogen at 105 °C. ^{31}P NMR spectroscopy initially showed the formation of equimolar quantities of trimethyl phosphate and the ylide, [(*dimethoxyphosphinyl*)(4-*methylphenyl*)*methylene*]*trismethoxy phosphorane* **4** (R = Me, X = 4-Me), $\delta_P(CDCl_3)$ 31.1 [d, J_{PP} 92, $P(O)(OMe)_2$] and 54.3 [d, J_{PP} 92, $P(OMe)_3$]; $\delta_C(CDCl_3)$ 28.6 (dd, J_{PC} 210 and 223, αC). However, as the reaction proceeded the ylide **4** (R = Me, X = 4-Me) was observed to rearrange to the bisphosphonate **5** (R = Me, X = 4-Me). After 4 h formation of the bisphosphonate was complete. The resulting yellow solution was then distilled (161 °C at 0.035 mmHg) to give the bisphosphonate **5** (R = Me, X = 4-Me) (3.0 g, 60%) as a white solid containing a small quantity of the bisphosphonate, *tetramethyl* (4-*methylphenyl*)*methane diphosphonate* **6** (R = Me, X = 4-Me). An analytically pure sample of the bisphosphonate **5** (R = Me, X = 4-Me) was isolated by reverse phase HPLC using methanol–water (60:40) as eluent, m.p. 59 °C, M^+, 336 (Found: C, 46.3; H, 6.7. $C_{13}H_{22}O_6P_2$ requires C, 46.43; H, 6.60%); $\delta_P(CDCl_3)$ 25.0; $\delta_C(CDCl_3)$ 17.0 (t, J_{PC} 7, Me), 20.8 (MeAr), 45.9 (t, J_{PC} 133, αC), 53.7 (t, J_{PC} 3, MeOP), 54.0 (t, J_{PC} 3, MeOP), 128.4 (t, J_{PC} 6, C-2, C-6), 128.6 (t, J_{PC} 2, C-3, C-5), 129.9 (t, J_{PC} 7, C-1) and 137.0 (t, J_{PC} 2, C-4); δ_H(100 MHz; $CDCl_3$) 1.93 (3 H, t, J_{PH} 16, Me), 2.34 (3 H, br s, MeAr), 3.62 (3 H, d, J_{PH} 11, MeOP), 3.74 (3 H, d, J_{PH} 11, MeOP), 7.18 (2 H, br, d, J_{HH} 8, 3-H, 5-H) and 7.66 (2 H, dt, J_{HH} 8, J_{PH} 2, 2-H, 6-H).

Tetramethyl 1-(4-*methoxyphenyl*)*ethane*-1,1-*diphosphonate* **5** (R = Me, X = 4-MeO). A stirred mixture of dimethyl 4-methoxybenzoylphosphonate (3.4 g, 14 mmol) and trimethyl phosphite (7.0 g, 56 mmol) was heated under dry nitrogen at 105 °C. ^{31}P NMR spectroscopy initially showed the formation of equimolar quantities of trimethyl phosphate and the ylide [(*dimethoxyphosphinyl*)(4-*methoxyphenyl*)*methylene*]*trismethoxyphosphorane* **4** (R = Me, X = 4-MeO); $\delta_P(CDCl_3)$ 30.7 [d, J_{PP} 95, $P(O)(OMe)_2$] and 53.9 [d, J_{PP} 95, $P(OMe)_3$]; $\delta_C(CDCl_3)$ 27.5 (dd, J_{PC} 211 and 224, αC)]. However, as the reaction proceeded the ylide **4** (R = Me, X = 4-MeO) was observed to rearrange to the bisphosphonate **5** (R = Me, X = 4-MeO). After 4 h formation of the bisphosphonate was complete. The resulting solution was then distilled (165 °C at 0.05 mmHg) to give the crude bisphosphonate **5** (R = Me, X = 4-MeO) which crystallized on cooling. Soluble impurities were removed by heating in diethyl ether. The bisphosphonate **5** (R = Me, X = 4-MeO) (2.85 g, 60%) was recovered as a white solid containing a small quantity of the bisphosphonate, *tetramethyl* (4-*methoxyphenyl*)*methanediphosphonate* **6** (R = Me, X = 4-MeO). An analytically pure sample of the bisphosphonate **5** (R = Me, X = 4-MeO) was isolated by reverse phase HPLC using methanol–water (60:40) as eluent, m.p. 81–82 °C; M^+, 352 (Found: C, 44.2; H, 6.25. $C_{13}H_{22}O_7P_2$ requires C, 44.32; H, 6.3%); $\delta_P(CDCl_3)$ 25.2; $\delta_C(CDCl_3)$ 17.2 (t, J_{PC} 7, Me), 45.5 (t, J_{PC} 133, αC), 53.7 (t, J_{PC} 3, MeOP), 54.1 (t, J_{PC} 3, MeOP), 55.0 (s, MeO), 113.3 (t, J_{PC} 2, C-3, C-5), 124.7 (t, J_{PC} 7, C-1), 129.9 (t, J_{PC} 6, C-2, C-6) and 158.7 (t, J_{PC} 2, C-4); δ_H(100 MHz; $CDCl_3$) 1.91 (3 H, t, J_{PH} 16, Me), 3.61 (3 H, d, J_{PH} 11, MeOP), 3.74 (3 H, d, J_{PH} 11, MeOP), 3.81 (3 H, s, MeO), 6.91 (2 H, br d, J_{HH} 9, 3-H, 5-H) and 7.71 (2 H, dt, J_{HH} 9, J_{PH} 2, 2-H, 6-H).

Tetramethyl 1-(4-*chlorophenyl*)*ethane*-1,1-*diphosphonate* **5** (R = Me, X = 4-Cl). A stirred mixture of dimethyl 4-chlorobenzoylphosphonate (3.5 g, 14 mmol) and trimethyl phosphite (7 g, 56 mmol) was heated under dry nitrogen at 105 °C. ^{31}P NMR spectroscopy initially showed formation of a little 4,5-*bis*(4-*chlorophenyl*)-4,5-*bis*(*dimethoxyphosphinyl*)-2,2,2-*triethoxy*-1,3,2-*dioxaphospholane* **7**, δ_P −48.1 (d, J_{PP} 25) and 17.9 (d, J_{PP} 25), together with equimolar quantities of trimethyl phosphate and the ylide, [(4-*chlorophenyl*)(*dimethoxyphosphinyl*)*trismethoxyphosphorane* **4** (R = Me, X = 4-Cl), δ_P 30.2 (d, J_{PP} 88, $P(O)(OMe)_2$] and 54.0 [d, J_{PP} 88, $P(OMe)_3$]; δ_C 28.2 (dd, J_{PC} 208 and 222]. However, as the reaction proceeded the ylide **4** (R = Me, X = 4-Cl) was observed to rearrange to the *bisphosphonate* **5** (R = Me, X = 4-Cl). After 4 h the reaction was complete. The resulting solution was then distilled (172 °C at 0.05 mmHg) to give a white solid which was shown by ^{31}P NMR spectroscopy to be the bisphosphonate **5** (R = Me, X = 4-Cl) (3.1 g, 62%) in a reasonably good state of purity. An analytically pure sample of the bisphosphonate **5** (R = Me, X = 4-Cl) was obtained as a waxy solid by reverse phase HPLC using methanol–water (60:40) as eluent, M^+, 356, 358 (Found: C, 40.55; H, 5.3. $C_{12}H_{19}ClO_6P_2$ requires C, 40.41; H, 5.37%); $\delta_P(CDCl_3)$ 25.2; $\delta_C(CDCl_3)$ 17.1 (t, J_{PC} 7, Me), 46.1 (t, J_{PC} 133, αC), 54.0 (t, J_{PC} 4, MeOP), 54.2 (t, J_{PC} 4, MeOP), 128.3 (t, J_{PC} 2, C-3, C-5), 130.2 (t, J_{PC} 6, C-2, C-6), 132.2 (t, J_{PC} 7, C-1) and 133.8 (t, J_{PC} 3, C-4): $\delta_H(CDCl_3)$ 1.91 (3 H, t, J_{PH} 16, Me), 3.63 (3 H, d, J_{PH} 11, MeOP), 3.75 (3 H, d, J_{PH} 11, MeOP), 7.34 (2 H, br d, J_{HH} 9, 3-H, 5-H) and 7.72 (2 H, dt, J_{HH} 9, J_{PH} 2, 2-H, 6-H).

Reactions of Dimethyl 2,4-*Dichlorobenzoylphosphonate* **1** (X = 2,4-Cl_2) *with Trimethyl Phosphite*.—(*a*) Dimethyl 2,4-dichlorobenzoylphosphonate **1** (X = 2,4-Cl_2) (2 g, 7 mmol) was mixed with trimethyl phosphite (1.75 g, 14 mmol) and the mixture left at room temperature. After 4 days ^{31}P NMR spectroscopy showed that about half the benzoylphosphonate had reacted and that trimethyl phosphate and the ylide [(2,4-dichlorophenyl)(dimethoxyphosphinyl)methylene)trismethoxyphosphorane **4** (R = Me, X = 2,4-Cl_2), had been produced $\delta_P(CDCl_3)$ 28.3 [d, J_{PP} 90, $P(O)(OMe)_2$] and 50.0 [d, J_{PP} 90, $P(OEt)_3$]; $\delta_C(CDCl_3)$ 25.6 (dd, J_{PC} 212 and 231, αC). There was no evidence for the formation of 4,5-bis(2,4-dichlorophenyl)-4,5-bis(dimethoxyphosphinyl)-2,2,2-trimethoxy-1,3,2-dioxaphospholane.

(*b*) Dimethyl 2,4-dichlorobenzoylphosphonate (2 g, 7 mmol) was mixed with trimethyl phosphite (1.75 g, 14 mmol) and the mixture heated at 85 °C for 2.5 days. ^{31}P NMR spectroscopy indicated that the reaction was complete and that trimethyl phosphate and the ylide, [(2,4-dichlorophenyl)(dimethoxyphosphinyl)methylene]trismethoxyphosphorane **4** (R = Me, X = 2,4-Cl_2), were the major products. Thermal rearrangement of the ylide **4** (R = Me, X = 2,4-Cl_2) to tetramethyl 1-(2,4-dichlorophenyl)ethane-1,1-diphosphonate **5** (R = Me, X = 2,4-Cl_2); $\delta_P(CDCl_3)$ 24.6 had occurred only to a minor extent (10%).

Reactions of Dimethyl Benzoylphosphonates **1** (X = OMe, H and Me) *with Triethyl Phosphite.*—[*(Dimethoxyphosphinyl)(4-methoxyphenyl)methylene*]*trisethoxyphosphorane* **4** (R = Et, X = 4-MeO). A stirred mixture of dimethyl 4-methoxybenzoylphosphonate (3 g, 14 mmol) and triethyl phosphite (3.5 g, 28 mmol) was heated, under dry nitrogen, at 85 °C for 10 h. ^{31}P NMR spectroscopy showed the formation of equimolar quantities of triethyl phosphate and the *ylide* **4** (R = Et, X = 4-MeO). The triethyl phosphate and other volatile material was removed by heating under reduced pressure to give the ylide in essentially quantitative yield (Found: C, 48.75; H, 7.1. $C_{16}H_{28}O_7P_2$ requires C, 48.73; H, 7.16%); $\delta_P(CDCl_3)$ 34.5 [d, J_{PP} 94, P(O)(OMe)$_2$] and 49.4 (d, J_{PP} 94, P(OEt)$_3$]; $\delta_C(CDCl_3)$ 16.0 (d, J_{PC} 7, Me), 28.6 (dd, J_{PC} 211 and 223, αC), 51.5 (d, J_{PC} 6, POMe), 55.0 (br s, OMe), 64.2 (d, J_{PC} 7, $POCH_2$), 113.3 (s, C-3, C-5), 127.8 (d, J_{PC} 5, C-1), 132.3 (dd, J_{PC} 6 and 8, C-2, C-6) and 156.2 (br s, C-4).

[*(Dimethoxyphosphinyl)(phenyl)methylene*]*trisethoxyphosphorane* **4** (R = Et, X = H). A stirred mixture of dimethyl benzoylphosphonate (3 g, 14 mmol) and triethyl phosphite (9.31 g, 28 mmol) was heated, under dry nitrogen at 85 °C for 10 h. ^{31}P NMR spectroscopy showed the formation of equimolar quantities of triethyl phosphate and the *ylide* (R = Et, X = H); $\delta_P(CDCl_3)$ 31.3 [d, J_{PP} 88, P(O)(OMe)$_2$] and 49.5 [d, J_{PP} 88, P(OEt)$_3$]; $\delta_C(CDCl_3)$ 30.9 (dd, J_{PC} 209 and 220, αC) as the major products.

[*(Dimethoxyphosphinyl)(4-methylphenyl)methylene*]*trisethoxyphosphorane* **4** (R = Et, X = 4-Me). A stirred mixture of dimethyl 4-methylbenzoylphosphonate (3 g, 14 mmol) and trimethyl phosphite (9.31 g, 28 mmol) was heated under dry nitrogen, at 85 °C for 10 h. ^{31}P NMR spectroscopy showed the formation of equimolar quantities of triethyl phosphate and the *ylide* **4** (R = Et, X = 4-Me); $\delta_P(CDCl_3)$ 31.6 [d, J_{PP} 91, P(O)(OMe)$_2$] and 49.7 [d, J_{PP} 91, P(OEt)$_3$]; $\delta_C(CDCl_3)$ 29.7 (dd, J_{PC} 210 and 221, αC) as the major products.

2-*Ethylbenzoic Acid.*—This compound was prepared from 1-bromo-2-ethylbenzene by carbonation of its Grignard reagent.[9] Recrystallisation of the product from water gave a white crystalline solid (6 g, 58%), m.p. 66 °C (lit.,[9] m.p. 65.5 °C) (Found: C, 72.15; H, 6.45. Calc. for $C_9H_{10}O_2$: C, 72.0; H, 6.7%); $\delta_C(CDCl_3)$ 15.9(q), 27.7(t), 125.8(d), 128.0(s), 130.4(d), 131.6(d), 133.0(d), 147.3(s) and 173.8(s); δ_H(270 MHz; $CDCl_3$) 1.27 (3 H, t, J_{HH} 8, Me), 3.07 (2 H, q, J_{HH} 8, CH_2), 7.22–7.37 (2 H, m, 3-H, 5-H), 7.45 (1 H, td, *J* 8 and 1.5, 4-H) and 8.05 (1 H, dd, *J* 8 and 1.5, 6-H).

Dimethyl 2-Ethylbenzoylphosphonate **8** (Y = CH_2).—2-Ethylbenzoic acid (9.5 g) was mixed with thionyl chloride (9.3 cm^3) and stirred overnight under dry nitrogen. Excess of thionyl chloride was then removed under reduced pressure. To the resulting oil under nitrogen was then slowly added trimethyl phosphite (7.9 g). When the reaction was complete the excess of phosphite was removed under reduced pressure and the residue distilled *in vacuo* to give the pure ester **8** (Y = CH_2) (12 g, 78%) as a colourless oil, b.p. 128–130 °C at 0.01 mmHg, M$^+$, 242 (Found: C, 54.4; H, 6.15. $C_{11}H_{15}PO_4$ requires C, 54.54; H, 6.24%); $\delta_P(CDCl_3)$ 0.7; $\delta_C(CDCl_3)$ 15.4 (Me), 26.9 (CH_2), 53.8 (d, J_{PC} 7, MeOP), 125.5 (C-5), 130.3 (d, J_{PC} 4, C-3), 131.9 (d, J_{PC} 2, C-6), 133.1 (C-4), 133.9 (d, J_{PC} 64, C-1), 145.6 (d, J_{PC} 10, C-2) and 200.4 (d, J_{PC} 171, C=O); $\delta_H(CDCl_3)$ 1.21 (3 H, t, *J* 7, Me), 2.89 (2 H, q, *J* 7, CH_2), 3.90 (6 H, d, J_{PH} 11, MeOP), 7.22–7.62 (3 H, m, 3-H, 4-H, 5-H) and 8.31–8.45 (1 H, m, 6-H).

Reaction of Dimethyl 2-Ethylbenzoylphosphonate **8** (Y = CH_2) *with Trimethyl Phosphite.*—Dimethyl 2-ethylbenzoylphosphonate **8** (Y = CH_2) (4 g) was heated at 106 °C in a nitrogen atmosphere with trimethyl phosphite (5 g) overnight. ^{31}P NMR spectroscopy indicated the formation of similar quantities of both *dimethyl indan-1-ylphosphonate* **10** (Y = CH_2) [$\delta_P(CDCl_3)$ 31.3] (*ca.* 40%) and the ylidic phosphonate **12** (Y = CH_2) {$\delta_P(CDCl_3)$ 29.3 [d, J_{PP} 98, P(O)(OMe)$_2$] and 50.5 [d, J_{PP} 98, P(OMe)$_3$]} (*ca.* 40%), in addition to trimethyl phosphate. Volatile components were removed by heating under reduced pressure (70 °C at 0.01 mmHg) and the major products were then isolated either by column chromatography on silica using ethyl acetate as the eluent, or by reverse phase HPLC using methanol–water (60:40) as eluent.

Dimethyl indan-1-ylphosphonate **10** (Y = CH_2) was isolated as a colourless liquid, M$^+$, 226 (Found: C, 58.45; H, 6.8. $C_{11}H_{15}O_3P$ requires C, 58.4; H, 6.68%); $\delta_P(CDCl_3)$ 31.3; $\delta_C(CDCl_3)$ 26.6 (d, J_{PC} 3, C-2), 31.7 (d, J_{PC} 4, C-3), 42.1 (d, J_{PC} 143, C-1), 52.7 (d, J_{PC} 7, MeOP), 53.1 (d, J_{PC} 7, MeOP), 124.6 (d, J_{PC} 2, C-4), 125.5 (d, J_{PC} 4, C-7), 126.4 (d, J_{PC} 3, C-5), 127.5 (d, J_{PC} 3, C-6), 137.9 (d, J_{PC} 6, C-3a) and 144.5 (d, J_{PC} 9, C-7a); δ_H(270 MHz; $CDCl_3$) 2.24–2.40 (2 H, m, 3-H), 2.84–2.92 (1 H, m, 2-H), 2.92–3.08 (1 H, m, 2-H), 3.56 (1 H, m, 1-H), 3.56 (3 H, d, J_{PH} 10, MeOP), 3.66 (3 H, d, J_{PH} 10, MeOP), 7.10–7.21 (3 H, m, Ar-H) and 7.37–7.48 (1 H, m, 7-H).

The [*(dimethoxyphosphinyl)(2-ethylphenyl)methylene*]*trismethoxyphosphorane* **12** (Y = CH_2) was isolated by reverse phase HPLC as its bisphosphonate decomposition product, *tetramethyl (2-ethylphenyl)methanediphosphonate* **6** (R = Me, X = 2-Et), M$^+$, 336 (Found: C, 46.7; H, 6.7. $C_{13}H_{22}O_6P_2$ requires C, 46.43; H, 6.60%); $\delta_P(CDCl_3)$ 21.9; $\delta_C(CDCl_3)$ 14.6 (Me), 26.1 (CH_2), 39.6 (t, J_{PC} 134, α-C), 53.4 (m, MeOP), 54.1 (m, MeOP), 125.9 (t, J_{PC} 3, C-5), 126.9 (t, J_{PC} 8, C-1), 128.0 (t, J_{PC} 3, C-3), 129.0 (t, J_{PC} 2, C-4), 130.3 (t, J_{PC} 4, C-6) and 142.6 (t, J_{PC} 8, C-2); δ_H(270 MHz; $CDCl_3$) 1.22 (3 H, t, J_{HH} 8, Me), 2.67 (2 H, q, J_{HH} 8, CH_2), 3.60 (6 H, d, J_{PH} 11, MeOP), 3.77 (6 H, d, J_{PH} 11, MeOP), 4.12 (1 H, t, J_{PH} 26, α-CH), 7.23 (3 H, m, 3-H, 4-H, 5-H) and 7.83 (1 H, m, J_{PH} 2, 6-H).

Reaction of Dimethyl 2-Methoxybenzoylphosphonate with Trimethyl Phosphite.—Samples of a mixture of dimethyl 2-methoxybenzoylphosphonate **8** (Y = O) (0.5 g, 2 mmol) and trimethyl phosphite (0.74 g, 6 mmol) were heated at various temperatures and the reactions monitored by ^{31}P NMR spectroscopy. In all cases two products, in addition to trimethyl phosphate, were formed, [(dimethoxyphosphinyl)(2-methoxyphenyl)methylene]trismethoxyphosphorane **12** (Y = O), {δ_P-($CDCl_3$) 31.4 [d, J_{PP} 94, P(O)(OMe)$_2$], 54.8 (d, J_{PP} 94, P(OMe)$_3$} and dimethyl 2,3-dihydrobenzo[*b*]furan-3-ylphosphonate **10** (Y = O) [$\delta_P(CDCl_3)$ 27.0], although the ratio of these products depended on the reaction temperature [at 105 °C the ratio of **12** (Y = O): **10** (Y = O) was 25:75, at 70 °C 46:54, and at 20 °C 80:20]. A sample of the reactant mixture (0.3 g) was also dissolved in dry toluene (5 g) and then heated at 105 °C for 7 h. Although the reaction was incomplete, ^{31}P NMR spectroscopy showed the formation of significant quantities of the phosphonate **10** (Y = O), but there was no evidence for the formation of any ylidic phosphonate **12** (Y = O).

Dimethyl 2,3-dihydrobenzofuran-3-ylphosphonate **10** (Y = O). A pure sample of the phosphonate **10** (Y = O) was obtained from one of the previous reaction mixtures by reverse phase HPLC using methanol–water (60:40) as eluent, M$^+$, 228; $\delta_P(CDCl_3)$ 27.0; $\delta_C(CDCl_3)$ 39.7 (d, J_{PC} 148, C-3), 52.9 (d, J_{PC} 7, MeOP), 53.6 (d, J_{PC} 7, MeOP), 71.1 (d, J_{PC} 3, C-2), 109.7 (d, J_{PC} 2, C-7), 120.7 (d, J_{PC} 3, C-5), 121.9 (d, J_{PC} 7, C-3a), 125.6 (d, J_{PC} 4, C-4), 129.2 (d, J_{PC} 3, C-6) and 160.1 (d, J_{PC} 8, C-7a); δ_H(270 MHz; $CDCl_3$) 3.6 (3 H, d, J_{PH} 11, MeOP), 3.7 (3 H, d, J_{PH} 11, MeOP), 3.8 (1 H, dt, J_{PH} 18, J_{HH} 9, 3-H), 4.68–4.80 (2 H, m, 2-H), 6.82 (1 H, d, J_{HH} 8, 7-H), 6.90 (1 H, t, J_{HH} 7, 5-H), 7.18 (1 H, br t, J_{HH} 8, 6-H) and 7.43 (1 H, d, J_{HH} 7, 4-H).

Reaction of Dimethyl 2-Phenylbenzoylphosphonate with Trimethyl Phosphite.—Dimethyl fluoren-9-ylphosphonate **15**. Dimethyl 2-phenylbenzoylphosphonate (5 g, 17 mmol) was heated under nitrogen with trimethyl phosphite (4.3 g, 35 mmol) at 85 °C for 3 h. ^{31}P NMR spectroscopy indicated the formation of the fluorenylphosphonate **15** (*ca.* 100%). The volatile components were removed from the reaction mixture by heating under reduced pressure (55 °C at 0.05 mmHg) to give a residue which solidified with time. Recrystallisation of the residue from diethyl ether gave the dimethyl fluoren-9-ylphosphonate **15** (4.1 g, 87%) as a white crystalline solid, m.p. 88 °C, M^+, 274 (Found: C, 65.4; H, 5.75. $C_{15}H_{15}O_3$ requires C, 65.69; H, 5.51%); $\delta_P(CDCl_3)$ 26.6; $\delta_C(CDCl_3)$ 46.4 (d, J_{PC} 137, C-9), 53.3 (d, J_{PC} 7, MeOP), 119.9 (d, J_{PC} 2, C-4, C-5), 126.1 (d, J_{PC} 3, C-1, C-8), 127.0 (d, J_{PC} 3, C-2, C-7), 127.9 (d, J_{PC} 2, C-3, C-6), 138.4 (d, J_{PC} 6, C-8a, C-9a) and 141.5 (d, J_{PC} 6, C-4a, C-5a); δ_H(270 MHz; $CDCl_3$) 3.53 (6 H, d, J_{PH} 11, Me), 4.54 (1 H, d, J_{PH} 30, 9-H), 7.3 (2 H, dt, J_{HH} 7 and 1, 2-H, 7-H), 7.42 (2 H, br t, J_{HH} 7, 3-H, 6-H), 7.78 (2 H, d, J_{HH} 7, 4-H, 5-H) and 7.84 (2 H, br d, J_{HH} 7, 1-H, 8-H).

Subsequent ^{31}P NMR studies showed that when a 3 molar excess of the trimethyl phosphite was used in the reaction it was complete after only 35 min at 90 °C, whilst at room temperature it took *ca.* 10 days. In both these reactions no evidence for the formation of the ylidic phosphonate **4** (R = Me, X = 4-Ph) was observed.

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