Reactions of carbene intermediates from the reaction of trialkyl phosphites with dialkyl benzoylphosphonates: intramolecular cyclisations of 2-substituted dialkyl benzoylphosphonates

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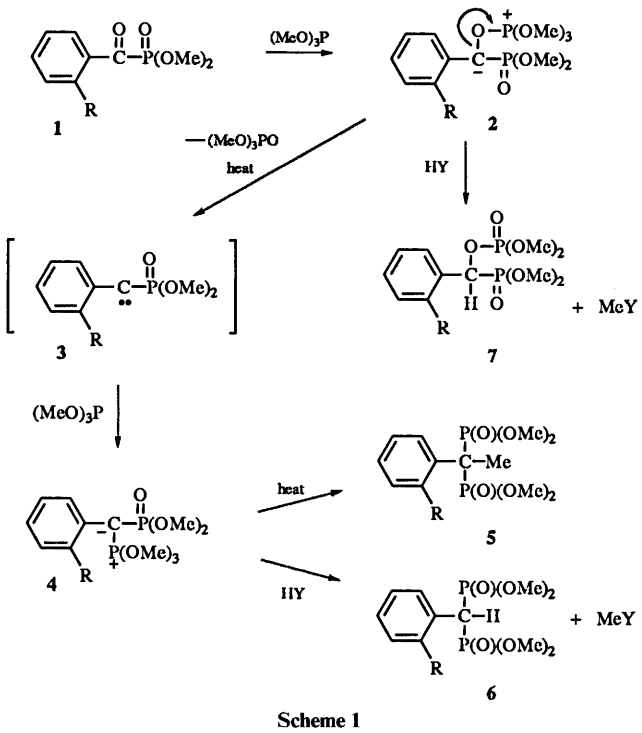
The reaction of dialkyl benzoylphosphonates 1 with trialkyl phosphites leads to the formation of carbene intermediates 3 *via* the anionic intermediates 2. The carbene intermediates 3 (R = 2-PhO, 2-PhOCH$_2$, and 2-PhS) have been generated by heating the corresponding 2-substituted dialkyl benzoylphosphonates with trimethyl phosphite and their subsequent reactions investigated. Reactions proceed either by intermolecular trapping of the carbene intermediates by trimethyl phosphite to give novel ylidic phosphonates 4, or by intramolecular routes involving carbene insertion into the π-system of the phenyl ring in the substituent. Studies using methyl-substituted derivatives have shown that the formation of the thioxanthenylphosphonate 15 (X = S, R′ = R″ = Me) proceeds *via* a spiro diene intermediate 14 (X = S, R′ = R″ = Me).

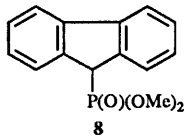
We have previously reported[1] that under appropriate conditions trialkyl phosphites react with dialkyl benzoylphosphonates **1** to give carbene intermediates **3** *via* the initially formed anionic intermediates **2** (Scheme 1). We have also shown that, when a suitable *ortho*-substituent is present on the benzene ring, the carbene intermediates can undergo intramolecular reactions involving the substituent, often leading to the formation of cyclic products.

Our initial studies were concerned largely with the reactions of the carbene centres in intermediates with saturated *ortho*-substituents.[2] These showed a strong preference for carbene insertion into a C–H bond on the substituent resulting in the formation of 5-membered ring systems, even in those cases where the formation of larger rings was possible. This preference for 5-membered ring formation was also observed in other *ortho*-substituted phenylcarbenes of type **3**, such as in the case of the 2-phenyl substituted system **1** (R = Ph)[1] where it was found that the carbene intermediate **3** (R = Ph) could be formed and cyclised to the fluorenylphosphonate **8** even under very mild conditions. Here, reaction proceeds *via* carbene insertion into an aromatic C–H bond to give the 5-membered ring system **8** as the sole product. We have also reported our studies on the preparation of the 2-benzoyl substituted system **1** (R = PhCO)[3] from the corresponding *pseudo*-acid chloride **9** (Scheme 2) and have shown that the carbene from this system also cyclises to give a 5-membered ring system **10** by reacting with the carbonyl group of the benzoyl substituent rather than the phenyl ring.

We have now investigated the reactions of a number of other carbene intermediates **12** where the spacer group, X, does not readily interact with the carbene centre. The carbenes **12** cannot therefore cyclise to give 5-membered ring systems by insertion into a C–H bond, and in this way, we hoped to encourage alternative reaction pathways.

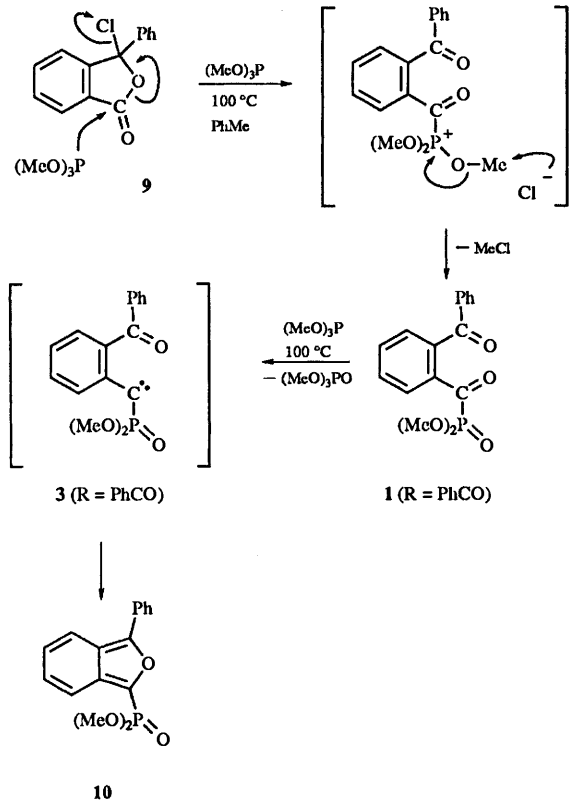


Scheme 1



Results and discussion

The 2-phenoxy substituted system **11** (X = O, R′ = R″ = H) was investigated first. Dimethyl 2-phenoxybenzoylphosphonate when heated with trimethyl phosphite gave several products in addition to trimethyl phosphate. The major product, giving a signal at δ_P 20.8 ppm in the ^{31}P NMR spectrum and typically accounting for some 60% of the fate of the benzoylphosphonate **11** (X = O, R′ = R″ = H), was shown to be the tricyclic system **17** (X = O, R′ = R″ = H). This presumably arises as a result of an initial carbene insertion into the π-system of the 2-phenoxy substituent to give **13** (X = O, R′ = R″ = H) followed by an appropriate rearrangement (Scheme 3). The destruction of the

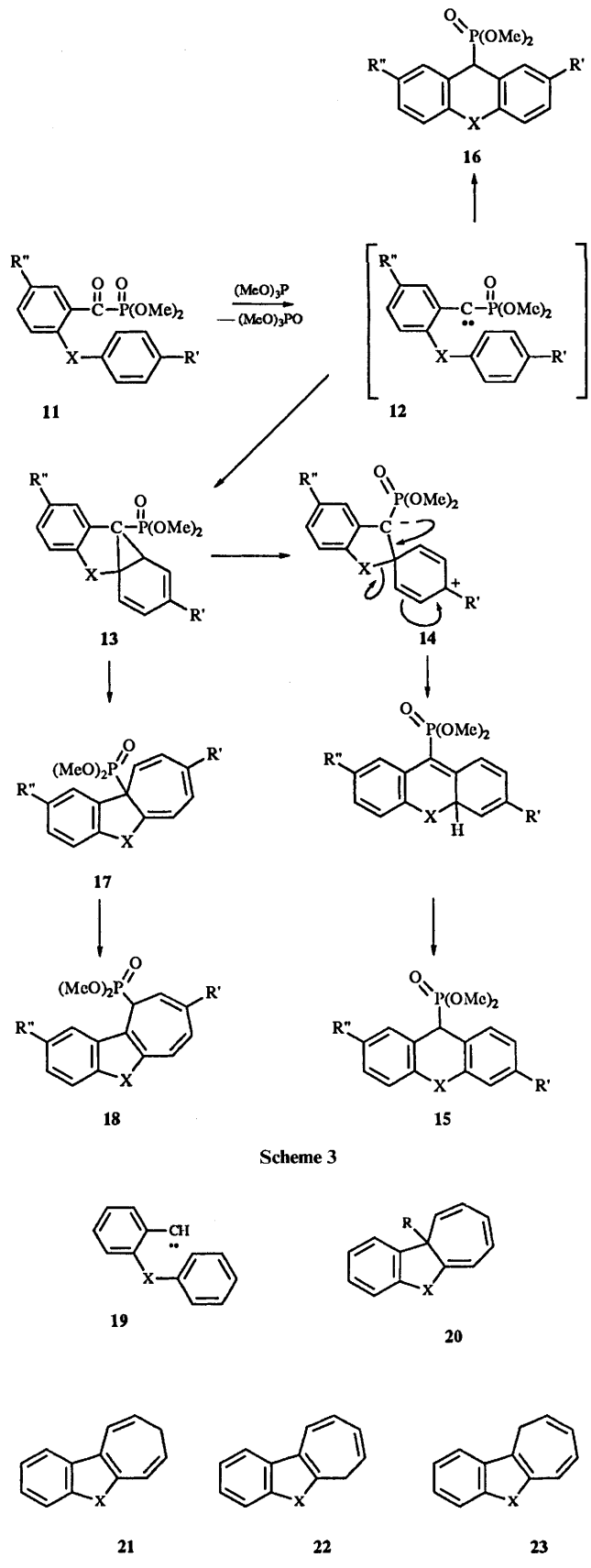


Scheme 2

aromaticity of the phenoxy substituent was readily apparent in the ^{1}H NMR spectrum of **17** (X = O, R′ = R″ = H) which contained only four aromatic proton resonances. A similar reaction pathway has been reported[4] for (2-phenoxyphenyl)-(phenyl)carbene, generated photochemically from (2-phenoxyphenyl)(phenyl)diazomethane, which led to the formation of **20** (X = O, R = Ph). However, in the case of 2-phenoxyphenylcarbene **19** (X = O), generated from the corresponding tosylhydrazone sodium salt at low pressure in the gas phase,[5] the initially formed cycloheptatrienyl system **20** (X = O, R = H) was not detected since it was found to undergo a 1,5-shift to give the more stable benzofuran system **21** (X = O) together with smaller quantities of the tautomeric forms **22** (X = O) and **23** (X = O). No thermal rearrangement was observed in the phosphonate-substituted cycloheptatriene system **17** (X = O, R′ = R″ = H), although it is interesting to note that the analogous phenyl-susbtituted system **20** (X = O, R = Ph)[4] undergoes photochemically induced rearrangements under appropriate conditions.

The second major pathway, accounting for about one third of the fate of the carbene intermediate **12** (X = O, R′ = R″ = H), involves an intermolecular trapping of the carbene intermediate by trimethyl phosphite. This results in the initial formation of the ylidic phosphonate **4** (R = PhO) with its characteristic ^{31}P NMR resonances [δ_P 53.5 (d, J_{PP} 93, $P(OMe)_3$) and 31.6 (d, J_{PP} 93, $P(OMe)_2$)], although some decomposition of this to the corresponding bisphosphonate **6** (R = PhO) is also observed.

The phosphate **7** (R = PhO) was also frequently observed among the reaction products and arises as a consequence of the initially formed anionic intermediate **2** (R = PhO) being trapped by proton donors, such as moisture, in the reaction mixture. This product has a very characteristic ^{31}P NMR spectrum [$\delta_P(CDCl_3)$ 19.4 (d, J_{PP} 34, $P(O)(OMe)_2$) and 1.5 (d, J_{PP} 34, $OP(O)(OMe)_2$)] and the amount formed during the reaction is very dependent on the care with which moisture is excluded from the reaction mixture. No evidence could be found for cyclisation of the carbene **12** (X = O, R′ = R″ = H) leading to the formation of a six-membered ring as in the



Scheme 3

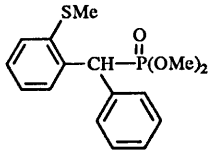
xanthenylphosphonate **15/16** (X = O, R′ = R″ = H), despite careful analysis of the ^{1}H NMR spectrum of the crude reaction mixture.

We next investigated the effects of replacing the oxygen bridging atom by a sulfur atom by preparing dimethyl 2-(phenylsulfanyl)benzoylphosphonate **1** (R = PhS) and investigating its reaction with trimethyl phosphite. Because the phosphonate **1** (R = PhS) showed a tendency to decompose

during distillation, it was later found that a cleaner reaction mixture could be obtained if the benzoylphosphonate **1** (R = PhS) was generated *in situ* in the presence of an excess of trimethyl phosphite. This was the approach used with the methyl-substituted analogues discussed later.

In contrast to the 2-phenoxy substituted case, the corresponding sulfur system **3** (R = PhS) showed intermolecular trapping of the carbene centre by trimethyl phosphite, leading to the initial formation of the ylidic phosphonate **4** (R = PhS), to now be the major pathway accounting for *ca.* 60% of the reaction product. This is probably the result of the phenyl ring in this sulfur system being less well orientated for interaction with the carbene centre although the phenyl ring in the sulfur system is also likely to be less activated to electrophilic attack. However, the phosphonates **15/16** (X = S, R′ = R″ = H) and **17** (X = S, R′ = R″ = H) were produced from the carbene intermediate **3** (R = PhS) as a result of an intramolecular carbene insertion into the *'ortho'* substituent and accounted for about one third of the reaction product. These components were produced in an approximately 2:1 ratio in favour of the six membered ring system **15/16** (X = S, R′ = R″ = H). A small quantity of the phosphate **7** (R = PhS) was also produced as a side reaction as a result of trapping of the anionic intermediate **2** (R = PhS).

During the isolation of these components by reverse-phase HPLC two other minor components, **24** and **25** (X = S, R = H), were isolated which are worthy of note. The route to the former system is not readily apparent although clearly involves several steps, while the latter results from the decomposition of the ylidic phosphonate **4** (R = PhS) and will be discussed elsewhere.



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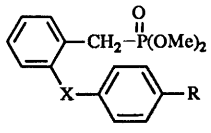

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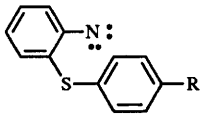
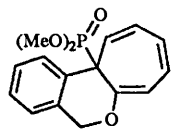


26

Interestingly, during the isolation of the cycloheptatrienyl system **17** (X = S, R′ = R″ = H) it was observed that some of an isomeric compound was sometimes produced. The mechanism of this process is not fully understood at present since on some occasions this rearrangement appeared to occur readily on heating, while on other occasions the **17** (X = S, R′ = R″ = H) appeared to be resistant to rearrangement under similar conditions. The ^{13}C NMR spectrum of the rearranged material clearly showed that the phosphorus had become attached to an sp^3 hybridised methine carbon (δ_C 38.4, d, J_{PC} 147, α-CH), while the ^1H NMR spectrum of the aromatic portion of the material showed shifts consistent with the formation of the 1-benzothiophene[6] ring system with both aromatic hydrogens adjacent to the bridgehead resonating at relatively low field (δ_H 7.71 and 7.78). In contrast, the material prior to rearrangement had shown one of these proton resonances, that on the benzene ring adjacent to the sulfur atom, at much higher field. This migration of the phosphonate group to facilitate the formation of an aromatic ring system was unexpected in view of our experience with the corresponding oxygen system **17** (X = O, R′ = R″ = H) but it is similar to that previously reported for **20** (X = S, R = H).[5] It should be noted, however, that it had been concluded that **20** (X = S) undergoes rearrangement to give the 8*H* isomer **21** (X = S) as the major tautomeric form. In contrast, the ^1H NMR spectrum of the rearranged product from **17** (X = S, R′ = R″ = H) clearly showed the four hydrogen atoms on the cycloheptatriene ring to be on adjacent carbon atoms with the phosphonate substituent being attached to one end of this sequence. We believe, therefore, that the phosphonate group has migrated during the rearrangement of **17** (X = O, R′ = R″ = H) to give the 10*H*-isomer **18** (X = O, R′ = R″ = H), although further work is needed to completely exclude the 6*H*-isomer. It may be of significance that the phenyl group in **20** (X = O, R = Ph) was found to migrate to the 10-position in a number of the products formed during its rearrangement under photochemical conditions.[4]

At first sight the cyclisation of the carbene intermediate **12** (X = S, R′ = R″ = H) to give the six-membered ring system **15** (X = S, R′ = R″ = H) would appear to proceed *via* carbene insertion into a C–H bond on the substituent's benzene ring. However, an alternative route *via* the spiro diene **14** (X = S, R′ = R″ = H) is feasible and has been observed in the analogous nitrene systems **26**.[7] To investigate this possibility the methyl-substituted system **11** (X = S, R′ = Me, R″ = H) was prepared and its reaction with trimethyl phosphite investigated. However, while this study showed that only one thioxanthenylphosphonate isomer was formed, the NMR spectra of this material did not allow us to make a completely unambiguous assignment of its structure. For this reason, we prepared the dimethyl-substituted system **11** (X = S, R′ = R″ = Me) and investigated its reaction with trimethyl phosphite. Here carbene insertion into the adjacent C–H bond on the substituent's benzene ring would result in the formation of the symmetrically substituted thioxanthenylphosphonate **16** (X = S, R′ = R″ = Me) whereas the route *via* the spiro diene **14** (X = S, R′ = R″ = Me) would result in the formation of the asymmetrically substituted system **15** (X = S, R′ = R″ = Me). Since the ^{13}C NMR spectrum of the product isolated showed 12 doublets in the aromatic region of the spectrum this confirmed its identity as the asymmetrically-substituted system **15** (X = S, R′ = R″ = Me) and hence that the reaction proceeds *via* the spiro diene mechanism. It is interesting to note that earlier workers[5] had concluded that systems such as 2-(phenylsulfanyl)phenylcarbene do not cyclise *via* a spiro diene mechanism.

Finally, we investigated the reaction of the 2-phenoxymethyl substituted system **1** (R = $PhOCH_2$). In this system the formation of 5-membered ring systems should be completely inhibited since even insertion into the π-system of the benzene ring would result in the formation of a six-membered ring system. As expected, intermolecular trapping to give the ylidic phosphonate **4** (R = $PhOCH_2$) proved to be the major reaction pathway from the carbene intermediate **3** (R = $PhOCH_2$), but a small quantity of a mono-phosphonate arising from an intramolecular trapping pathway was isolated from the reaction product. This material was readily identified as the phosphonate **27** by comparison with the ^1H NMR spectrum of



27

17 (X = O, R′ = R″ = H). The formation of the phosphonate **27** confirms that, in the absence of other available reaction pathways, the carbene centre can interact with the π-system of a phenyl ring, as in **3** (R = $PhOCH_2$), to give a six-membered heterocyclic ring system. Work is continuing on the reactions of

carbenes generated from other 2-substituted benzoylphosphonates.

Experimental

Dimethyl 2-phenoxybenzoylphosphonate 1 (R = PhO)
A mixture of 2-phenoxybenzoic acid (10 g, 47 mmol) and thionyl chloride (30 cm^3) was stirred under an atmosphere of dry nitrogen overnight after which the excess of thionyl chloride was removed under reduced pressure. To the residue, under nitrogen, was added dry toluene (20 cm^3) followed by trimethyl phosphite (5.8 g, 47 mmol). When the reaction was complete, the resulting mixture was distilled *in vacuo* (bp 182 °C at 0.02 mmHg) to give the title compound in essentially quantitative yield as a pale yellow oil, M^+, 306 (Found: C, 58.6; H, 4.9. $C_{15}H_{15}O_5P$ requires C, 58.83; H, 4.94%); $\delta_P(CDCl_3)$ 0.4; δ_H(270 MHz; $CDCl_3$) 3.82 (6 H, d, J_{PH} 11, POMe), 6.90 (1 H, d, J_{PH} 8, 3-H), 7.11–7.22 (4 H, m, 3-H, 2′-H, 4′-H, 6′-H), 7.38 (2 H, m, 3′-H, 5′-H), 7.48 (1 H, ddd, J_{HH} 2, 7.5 and 8, 4-H) and 7.98 (1 H, dd, J_{HH} 2 and 8, 6-H); $\delta_C(CDCl_3)$ 54.1 (×2) (d, J_{PC} 7, POMe), 118.2 (d, J_{PC} 1.5, C-3), 119.8 (×2) (s, C-2′, C-6′), 123.0 (s, C-4′), 124.3 (s, C-5), 128.3 (d, J_{PC} 62, C-1), 129.9 (×2) (s, C-3′, C-5′), 131.1 (d, J_{PC} 1, C-6), 135.1 (s, C-4), 155.8 (s, C-1′), 157.3 (d, J_{PC} 1.5, C-2) and 199.4 (d, J_{PC} 182, C=O). If distillation of **1** (R = PhO) is attempted at higher pressures, some decomposition to give xanthone occurs.

Reaction of dimethyl 2-phenoxybenzoylphosphonate with trimethyl phosphite
The phosphonate **1** (R = PhO) (3.0 g, 10 mmol) was heated under nitrogen with trimethyl phosphite (2.48 g, 20 mmol) at 100 °C for 1.5 h. Analysis of the resulting reaction mixture by ^{31}P NMR spectroscopy indicated that the major products, other than trimethyl phosphate, were the phosphonate **17** (X = O, R′ = R″ = H) (60%) and the ylidic phosphonate **4** (R = PhO) and its decomposition product **6** (R = PhO) (30%). A small quantity of the phosphate **7** (R = PhO) (10%) was also formed. The reaction mixture was heated under reduced pressure (60 °C at 0.3 mmHg) to remove the volatile components and the residue was subjected to reverse phase HPLC using a Dynamax C-18 column with aqueous methanol 60% as the eluent to give the following compounds.

10a-Dimethoxyphosphinoyl-10a*H*-benzo[*b*]cyclohepta[*d*]-furan 17 (X = O, R′ = R″ = H). This compound was isolated as a yellow solid, M^+, 290, mp 78 °C (Found: C, 61.9; H, 5.4. $C_{15}H_{15}O_4P$ requires C, 62.07; H, 5.17%); $\delta_P(CDCl_3)$ 20.8; δ_H(270 MHz; $CDCl_3$) 3.37 (3 H, d, J_{PH} 10.5, POMe), 3.58 (3 H, d, J_{PH} 10.5, POMe), 5.13–5.25 (1 H, m, J_{PH} 5, 8-H), 6.08–6.21 (4 H, m, 9-H, 10-H, 11-H, 12-H), 6.92 (1 H, d, J_{HH} 9, 6-H), 7.04 (1 H, td, J_{HH} 8 and 1, 4-H), 7.24 (1 H, m, 5-H) and 7.56 (1 H, dm, J_{HH} 8, 3-H); $\delta_C(CDCl_3)$ 53.96 (d, J_{PC} 7, POMe), 54.04 (d, J_{PC} 7, POMe), 54.7 (d, J_{PC} 153, CP), 102.9 (d, J_{PC} 8, CH), 109.6 (d, J_{PC} 2, CH), 117.2 (d, J_{PC} 3, CH), 122.7 (d, J_{PC} 3, CH), 125.2 (d, J_{PC} 3, CH), 125.3 (s, CH), 126.6 (d, J_{PC} 2, CH), 128.4 (d, J_{PC} 7, C), 128.5 (d, J_{PC} 6, CH), 129.4 (d, J_{PC} 3, CH), 147.9 (d, J_{PC} 4, q) and 156.3 (d, J_{PC} 6, q).

Tetramethyl (2-phenoxyphenyl)methane-1,1-diphosphonate 6 (R = PhO). The ylide **4** (R = PhO) {δ_P 53.5 [d, J_{PP} 93, $P(OMe)_3$] and 31.6 [d, J_{PP} 93, $P(OMe)_2$]} was isolated as its decomposition product **6** (R = PhO) as an oil, M^+ 400 (Found: C, 51.2; H, 5.35. $C_{17}H_{22}O_7P_2$ requires C, 51.01; H, 5.54%); $\delta_P(CDCl_3)$ 21.8; δ_H(270 MHz; $CDCl_3$) 3.70 (6 H, d, J_{PH} 11, POMe), 3.79 (6 H, d, J_{PH} 11, POMe), 4.66 (1 H, t, J_{PH} 25, αCH), 6.87 (1 H, dm, J_{HH} 8, 3-H), 6.99 (2 H, dm, J_{HH} 8.5, 2′-H, 6′-H), 7.12 (1 H, m, 5-H), 7.14 (1 H, m, 4′-H), 7.24 (1 H, m, 4-H), 7.33 (2 H, m, J_{HH} 7.5 and 8.5, 3′-H, 5′-H) and 7.89 (1 H, dq, J_{HH} 8 and 2, J_{PH} 2, 6-H); $\delta_C(CDCl_3)$ 35.5 (t, J_{PC} 135, αC), 53.6 (m, POMe), 53.9 (m, POMe), 118.5 (br s, CH), 118.8 (×2) (s, C-2′, C-6′), 120.8 (t, J_{PC} 7.5, C-1), 123.5 (t, J_{PC} 2, CH), 123.6 (s, C-4′), 129.1 (t, J_{PC} 2, CH), 129.7 (×2) (s, C-3′, C-5′), 131.3 (t, J_{PC} 4, CH), 154.7 (t, J_{PC} 8, C-2) and 156.9 (s, C-1′).

[(Dimethoxyphosphinoyl)(2-phenoxyphenyl)methyl] dimethyl phosphate 7 (R = PhO). This compound was isolated as a colourless oil, M^+, 416 (Found: C, 49.3; H, 5.6. $C_{17}H_{22}O_8P_2$ requires C, 49.05; H, 5.33%); $\delta_P(CDCl_3)$ 19.4 [d, J_{PP} 34, $P(O)(OMe)_2$] and 1.5 [d, J_{PP} 34, $OP(O)(OMe)_2$]; δ_H(270 MHz; $CDCl_3$) 3.59 (3 H, d, J_{PH} 11.5, POMe), 3.66 (3 H, d, J_{PH} 10.5, POMe), 3.66 (3 H, d, J_{PH} 11.5, POMe), 3.75 (3 H, d, J_{PH} 10.5, POMe), 6.16 (1 H, dd, J_{PH} 11 and 13, αCH), 6.76 (1 H, br d, J_{HH} 8, 3-H), 6.96–7.12 (4 H, m, 5-H, 2′-H, 4′-H, 6′-H), 7.21 (1 H, m, 4-H), 7.29 (2 H, m, 3′-H, 5′-H) and 7.66 (1 H, dt, J_{HH} 8 and 2, J_{PH} 2, 6-H); $\delta_C(CDCl_3)$ 53.8 (d, J_{PC} 7, POMe), 54.1 (d, J_{PC} 7, POMe), 54.4 (d, J_{PC} 6, POMe), 54.5 (d, J_{PC} 6, POMe), 68.1 (dd, J_{PC} 7 and 176, αC), 117.6 (d, J_{PC} 2, CH), 119.6 (×2) (s, C-2′, C-6′), 123.2 (d, J_{PC} 2, CH), 123.8 (s, C-4′), 124.3 (s, C-1), 129.3 (d, J_{PC} 4, CH), 129.8 (×2) (s, C-3′, C-5′), 130.2 (d, J_{PC} 2, CH), 154.8 (d, J_{PC} 7, C-2) and 156.5 (s, C-1′).

Dimethyl 2-(phenylsulfanyl)benzoylphosphonate 1 (R = PhS)
Thionyl chloride (10 cm^3) was added to 2-phenylsulfanylbenzoic acid [8] (0.26 g, 1.13 mmol) and the mixture stirred overnight under an atmosphere of dry nitrogen. The excess of thionyl chloride was then removed under reduced pressure and the residue, under nitrogen, was slowly treated with trimethyl phosphite (0.15 g, 1.2 mmol). When the reaction was complete, the resulting mixture was distilled under reduced pressure (bp 125 °C at 0.01 mmHg) to give the title compound (0.32 g, 90%) as a pale yellow oil in a good state of purity. Extreme care was needed to avoid significant decomposition of the benzoylphosphonate during distillation and minor impurities introduced as a result of the distillation prevented satisfactory combustion analysis; $\delta_P(CDCl_3)$ 1.0; $\delta_C(CDCl_3)$ 54.5 (×2) (d, J_{PC} 7, POMe), 124.3 (s, C-4′), 127.4 (d, J_{PC} 2, C-H), 129.5 (s, C-5), 129.9 (×2) (s, C-3′, C-5′), 131.4 (d, J_{PC} 66, C-1), 131.6 (s, C-1′), 133.8 (s, C-4), 134.0 (d, J_{PC} 3, C-6), 135.6 (×2) (s, C-2′, C-6′), 135.7 (s, C-1′), 145.0 (d, J_{PC} 10, C-2) and 197.6 (d, J_{PC} 175, C=O); δ_H(270 MHz, $CDCl_3$) 3.96 (6 H, d, J_{PH} 11, POMe), 6.86 (1 H, dm, J_{HH} 8, 3-H), 7.23 (1 H, m, 5-H), 7.30 (1 H, m, 4-H), 7.41–7.50 (3 H, m, 2′-H, 4′-H, 6′-H), 7.51–7.58 (2 H, m, 3′-H, 5′-H) and 8.59 (1 H, dd, J_{HH} 2 and 7.5, 6-H).

Reaction of dimethyl 2-(phenylsulfanyl)benzoylphosphonate with trimethyl phosphite
Dimethyl 2-(phenylsulfanyl)benzoylphosphonate (0.24 g, 0.96 mmol) was heated, under dry nitrogen, with trimethyl phosphite (0.36 g, 2.8 mmol) at 100 °C for 5 h. Analysis of the resulting orange reaction mixture by ^{31}P NMR spectroscopy indicated that the major products arising from the carbene intermediate **3** (R = PhS) were the ylidic phosphonate **4** (R = PhS) and its decomposition product **6** (R = PhS) (58%), and the phosphonates **16** (X = S, R′ = R″ = H) (21%) and **17** (X = S, R′ = R″ = H) (12%). A small quantity (*ca.* 9%) of the phosphate **7** (R = PhS) was also present in the reaction mixture. The reaction mixture was heated under reduced pressure (85 °C at 0.01 mmHg) to remove the volatile components and the residue was subjected to reverse phase HPLC using a Dynamax C-18 column with aqueous methanol (70%) as the eluent to give the following compounds.

[(Dimethoxyphosphinoyl)(2-phenylsulfanylphenyl)methyl] dimethyl phosphate 7 (R = PhS). This compound was isolated as a white solid, mp 125 °C, M^+, 432 (Found: C, 47.6; H, 5.3. $C_{17}H_{22}O_7P_2S$ requires C, 47.23; H, 5.13%); $\delta_P(CDCl_3)$ 1.6 [d, J_{PP} 34, $OP(O)(OMe)_2$] and 19.1 [d, J_{PP} 34, $P(O)(OMe)_2$]; δ_H(270 MHz; $CDCl_3$) 3.64 (3 H, d, J_{PH} 11, MeOP), 3.68 (3 H, d, J_{PH} 10.5, MeOP), 3.69 (3 H, d, J_{PH} 11, MeOP), 3.82 (3 H, d, J_{PH} 10.5, MeOP), 6.49 (1 H, dd, J_{PH} 11 and 13, αCH), 7.18–7.39 (8 H, m, 3-H, 4-H, 5-H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H) and 7.77 (1 H, m, 6-H); $\delta_C(CDCl_3)$ 53.9 (d, J_{PC} 7, MeOP), 54.2 (d, J_{PC} 7, MeOP), 54.3 (d, J_{PC} 6, MeOP), 54.5 (d, J_{PC} 6, MeOP), 71.2 (dd,

J_{PC} 7 and 174, αCH), 127.0 (s, C-4′), 128.1 (d, J_{PC} 2, C-5), 128.9 (d, J_{PC} 4, C-6), 129.1 (×2) (s, C-3′, C-5′), 129.7 (d, J_{PC} 2, CH), 130.8 (×2) (s, C-2′, C-6′), 134.1 (s, CH), 135.1 (d, J_{PC} 7, C-2), 135.3 (br s, C-1) and 136.4 (s, C-1′).

Tetramethyl [2-(phenylsulfanyl)phenyl]methane-1,1-diphosphonate 6 (R = PhS). The ylide **4** (R = SPh) {δ_P 50.6 [d, J_{PP} 93, $P(OMe)_3$] and 29.6 [d, J_{PP} 93, $P(OMe)_2$]} was isolated as its decomposition product **6** (R = SPh) as an oil, M^+, 416.0613; $\delta_P(CDCl_3)$ 21.3; δ_H(270 MHz; $CDCl_3$) 3.63 (6 H, d, J_{PH} 11, POMe), 3.77 (6 H, d, J_{PH} 11, POMe), 5.10 (1 H, t, J_{PH} 25, α-CH), 7.15–7.30 (6 H, m, ArH), 7.37 (1 H, td, J_{HH} 7.5 and 1, 5-H), 7.49 (2 H, d, J_{HH} 7.5, 3-H) and 7.98 (1 H, dm, J_{HH} 7.5, 6-H); $\delta_C(CDCl_3)$ 40.9 (t, J_{PC} 134, αC), 53.6 (m, POMe), 53.9 (m, POMe), 126.5 (s, C-4′), 128.7 (t, J_{PC} 3, CH), 128.8 (t, J_{PC} 3, CH), 129.0 (×2) (s, C-3′, C-5′), 129.4 (×2) (s, C-2′, C-6′), 131.0 (t, J_{PC} 4, C-6), 132.6 (t, J_{PC} 7, C-1), 134.8 (t, J_{PC} 9, C-2), 135.6 (t, J_{PC} 2, C-4) and 136.6 (s, C-1′).

Dimethyl 9*H*-thioxanthen-9-ylphosphonate 16 (X = S, R′ = R″ = H). This compound was isolated as a white solid, mp 118 °C, M^+, 306 (Found: C, 58.8; H, 4.75. $C_{15}H_{15}O_3PS$ requires C, 58.82; H, 4.94%); $\delta_P(CDCl_3)$ 24.2; δ_H(270 MHz; $CDCl_3$) 3.53 (6 H, d, J_{PH} 10.5, POMe), 4.72 (1 H, d, J_{PH} 28, 9-H), 7.22–7.28 (4 H, m, ArH) and 7.32–7.38 (4 H, m, ArH); $\delta_C(CDCl_3)$ 48.8 (d, J_{PC} 137, C–P), 53.5 (×2) (d, J_{PC} 7, POMe), 126.5 (d, J_{PC} 3, CH), 126.7 (d, J_{PC} 3, CH), 127.8 (d, J_{PC} 4, CH), 128.9 (d, J_{PC} 7, q), 130.6 (d, J_{PC} 5, CH) and 132.5 (d, J_{PC} 6, q).

10a-Dimethoxyphosphinoyl-10a*H*-cyclohepta[*b*][1]benzothiophene 17 (X = S, R′ = R″ = H). This compound was isolated as a yellow oil, M^+, 306.0480; $\delta_P(CDCl_3)$ 22.9; δ_H(270 MHz; $CDCl_3$) 3.42 (3 H, d, J_{PH} 10.5, POMe), 3.65 (3 H, d, J_{PH} 10.5, POMe), 5.18–5.25 (1 H, m, 6-H), 6.20–6.46 (4 H, m, 7-H, 8-H, 9-H, 10-H), 7.19–7.30 (3 H, m, 2-H, 3-H, 4-H) and 7.68 (1 H, dm, J_{HH} 7, 1-H); $\delta_C(CDCl_3)$ 53.86 (d, J_{PC} 8, POMe), 54.1 (d, J_{PC} 8, POMe), 61.6 (d, J_{PC} 147, C–P), 119.5 (d, J_{PC} 4, CH), 120.0 (d, J_{PC} 9, CH), 121.1 (d, J_{PC} 2, CH), 125.1 (d, J_{PC} 3, CH), 126.7 (s, CH), 126.9 (d, J_{PC} 4, CH), 128.0 (d, J_{PC} 6, CH), 128.7 (d, J_{PC} 3, CH), 129.2 (d, J_{PC} 3, CH), 133.8 (d, J_{PC} 5, q), 138.6 (d, J_{PC} 8, q) and 140.6 (d, J_{PC} 6, q).

Dimethyl α-(2-methylsulfanylphenyl)benzylphosphonate 24. A very small quantity of this compound was isolated as a colourless oil, M^+, 322 (Found: C, 59.9; H, 5.9. $C_{16}H_{19}O_3PS$ requires C, 59.63; H, 5.90%); $\delta_P(CDCl_3)$ 28.0; δ_H(270 MHz; $CDCl_3$) 2.40 (3 H, s, SMe), 3.56 (3 H, d, J_{PH} 11, POMe), 3.58 (3 H, d, J_{PH} 11, POMe), 5.25 (1 H, d, J_{PH} 26, αCH), 7.22–7.36 (6 H, m, ArH), 7.54 (2 H, dm, J_{HH} 7, 2′-H, 6′-H) and 8.04 (1 H, m, 6-H); $\delta_C(CDCl_3)$ 17.2 (s, SMe), 46.1 (d, J_{PC} 140, α-C), 53.4 (d, J_{PC} 7, POMe), 53.5 (d, J_{PC} 7, POMe), 125.9 (s, C-4′), 127.2 (d, J_{PC} 2, C-3′), 128.0 (s, C-2′), 128.1 (s, CH), 128.6 (×2) (s, CH), 129.7 (d, J_{PC} 3, CH), 129.8 (×2) (s, CH), 135.7 (d, J_{PC} 4, q), 135.9 (d, J_{PC} 5, q) and 137.8 (d, J_{PC} 13, q).

Dimethyl 2-(phenylsulfanyl)benzylphosphonate 25 (X = S, R = H). This compound, later shown to be a decomposition product of the ylide **4** (R = PhS), was isolated as a colourless oil, M^+, 308 (Found: C, 58.6; H, 4.9. $C_{15}H_{17}O_3PS$ requires C, 58.43; H, 5.56%); $\delta_P(CDCl_3)$ 28.9; δ_H(270 MHz; $CDCl_3$) 3.51 (2 H, d, J_{PH} 22, α-CH_2), 3.68 (6 H, d, J_{PH} 11, POMe), 7.16–7.23 (6 H, m, ArH), 7.30 (1 H, td, J_{HH} 7.5 and 1, 5-H), 7.39 (1 H, d, J_{HH} 7.5, 3-H) and 7.50 (1 H, dm, J_{HH} 7.5, 6-H); $\delta_C(CDCl_3)$ 30.6 (d, J_{PC} 139, αC), 52.9 (×2) (d, J 7, POMe), 126.4 (s, C-4′), 128.1 (d, J_{PC} 3, CH), 128.4 (d, J_{PC} 3, CH), 129.1 (×2) (s, C-3′, C-5′), 129.3 (×2) (s, C-2′, C-6′), 131.2 (d, J_{PC} 5, C-6), 133.9 (d, J_{PC} 9, q), 134.3 (t, J_{PC} 8, q), 134.6 (d, J_{PC} 3, CH) and 136.7 (br s, C-1′),

10-Dimethoxyphosphinoyl-10*H*-cyclohepta[*b*][1]benzothiophene 18 (X = S, R′ = R″ = H). This compound, which arose from the rearrangement of **17** (X = S, R′ = R″ = H), was isolated as a yellow oil, M^+, 306; $\delta_P(CDCl_3)$ 25.5; δ_H(270 MHz; $CDCl_3$) 3.52 (3 H, d, J_{PH} 11, POMe), 3.61 (3 H, d, J_{PH} 11, POMe), 4.68 (1 H, dd, J_{HH} 9, J_{PH} 27, 10-H), 5.60 (1 H, dt, J_{HH} 9 and 11, J_{PH} 9, 9-H), 6.24 (1 H, ddd, J_{HH} 11 and 6.5, J_{PH} 6, 8-H), 6.37 (1 H, dd, J_{HH} 11.5 and 6.5, 7-H), 6.79 (1 H, d, J_{HH} 11.5, 6-H), 7.22–7.43 (2 H, m, 2-H, 3-H), 7.71 (1 H, d, J_{HH} 8, 4-H) and 7.78 (1 H, d, J_{HH} 7.5, 1-H).

2-(4′-Methylphenylsulfanyl)benzoic acid

Anthranilic acid (2.0 g, 14.6 mmol) was added to a solution of concentrated hydrochloric acid (3.1 cm^3) in water (15 cm^3) and the mixture cooled to 5 °C. A cold (5 °C) solution of sodium nitrite (1.0 g, 14.6 mmol) in water (2 cm^3) was added dropwise to the mixture which was then stirred for 30 min at 5 °C. After this it was added dropwise to a cooled solution (5 °C) of toluene-*p*-thiol (1.81 g, 14.6 mmol) in aqueous sodium hydroxide (10 mol dm^{-3}; 50 cm^3) under nitrogen. The resulting mixture was extracted with ether (2 × 30 cm^3) and the extracts were discarded. The aqueous layer was then acidified using concentrated hydrochloric acid and re-extracted with ether (2 × 50 cm^3). The combined ether extracts were dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a light brown solid. This was washed repeatedly with light petroleum and then recrystallised from aqueous ethanol to give the title acid (2.5 g, 70%) as a light brown solid, mp 215 °C (lit.,[9] mp 215–216 °C) (Found: C, 68.6; H, 4.9. Calc. for $C_{14}H_{12}O_2S$: C, 68.84; H, 4.96%); $\delta_H(CDCl_3$; 90 MHz) 2.35 (3 H, s, Me), 6.69 (1 H, dd, J_{HH} 7.8 and 1.2, 3-H), 7.07–7.47 (6 H, m, 2′-H, 6′-H, 3′-H, 5′-H, 4-H, 5-H) and 7.94 (1 H, dd, J_{HH} 7.5 and 1.8, 6-H); $\delta_C(CDCl_3)$ 20.8 (Me), 124.4 (CH), 126.5 (CH), 127.3 (q), 128.4 (q), 130.7 (×2) (CH), 130.8 (CH), 132.3 (CH), 135.3 (×2) (CH), 139.2 (q), 142.4 (q) and 167.4 (C=O).

Preparation of dimethyl 2-(4′-methylphenylsulfanyl)benzoylphosphonate 11 (X = S, R′ = Me, R″ = H) *in situ* and its reaction with trimethyl phosphite

Thionyl chloride (15 cm^3) was slowly added to 2-(4′-methylphenylsulfanyl)benzoic acid (1.3 g, 5.3 mmol) in dry ether (5 cm^3) and the mixture stored overnight under nitrogen. The volatile components were removed under reduced pressure to give 2-(4′-methylphenylsulfanyl)benzoyl chloride as a brown oil which was used immediately without purification. To this acid chloride was added trimethyl phosphite (1.98 g, 15.9 mmol) and, after a short time, the resulting mixture was heated for 3 h at 100 °C under nitrogen. Analysis of this reaction mixture by ^{31}P NMR spectroscopy indicated the initial formation of the title ester **11** (X = S, R′ = Me, R″ = H) (δ_P 1.0) which then reacted further to give several products, the major ones being the ylidic phosphonate **4** (R = 4-MeC_6H_4), its decomposition product **6** (R = 4-MeC_6H_4) (63%) and the cyclic phosphonate **15** (X = S, R′ = Me, R″ = H) (10%). The reaction mixture was heated under reduced pressure (80 °C at 0.01 mmHg) to remove the volatile components, those remaining in the residue being isolated by reverse phase HPLC using methanol–water (70:30) as eluent.

Tetramethyl [2-(4′-methylphenylsulfanyl)phenyl]methane-1,1-diphosphonate 6 (R = 4-MeC_6H_4S). The ylide **4** (R = 4-MeC_6H_4S) {δ_P 29.8 [d, J_{PP} 93, $P(O)(OMe)_2$] and 50.9 [d, J_{PP} 93, $P(OMe)_3$]} was isolated as its decomposition product **6** (R = 4-MePhS) as a colourless oil, M^+, 430 (Found: C, 50.5; H, 5.93. $C_{18}H_{24}O_6P_2S$ requires C, 50.22; H, 5.62%); $\delta_P(CDCl_3)$ 21.3; δ_H(270 MHz; $CDCl_3$) 2.31 (3 H, m, Me), 3.64 (6 H, d, J_{PH} 11, MeOP), 3.79 (6 H, d, J_{PH} 11, POMe), 5.08 (1 H, t, J_{PH} 25, αCH), 7.08 (2 H, m, J_{HH} 8, 3′-H, 5′-H), 7.16 (2 H, m, J_{HH} 8, 2′-H, 6′-H), 7.23 (1 H, tm, J_{HH} 8, 4-H), 7.32 (1 H, tm, J_{HH} 8, 5-H), 7.39 (1 H, dm, J_{HH} 8, 3-H) and 7.95 (1 H, dm, J_{HH} 8, 6-H); $\delta_C(CDCl_3)$ 21.0 (s, Me), 40.8 (t, J_{PC} 134, αCH), 53.7 (×2) (m, MeOP), 53.9 (×2) (m, MeOP), 128.0 (t, J_{PC} 3, CH), 128.7 (t, J_{PC} 3, CH), 129.9 (×2) (s, C-2′, C-6′), 130.6 (×2) (s, C-3′, C-5′), 130.9 (t, J_{PC} 4, C-6), 131.5 (t, J_{PC} 7, C-1), 132.4 (s, C-1′), 134.4 (br s, C-4), 136.1 (d, J_{PC} 7, C-2) and 137.0 (s, C-4′).

Dimethyl 3-methyl-9*H*-thioxanthen-9-ylphosphonate 15 (X = S, R′ = Me, R″ = H). This compound was isolated as a light brown solid, M^+, 320.0638; $\delta_P(CDCl_3)$ 24.4; δ_H(270 MHz;

$CDCl_3$) 2.32 (3 H, d, J_{PH} 2, Me), 3.54 (6 H, d, J_{PH} 10.5, POMe), 4.68 (1 H, d, J_{PH} 28, 9-H), 7.04 (1 H, dm, J_{HH} 8, 2-H), 7.18 (1 H, s, 4-H), 7.20–7.28 (3 H, m, 1-H, 5-H, 7-H) and 7.35 (2 H, m, 6-H, 8-H); $\delta_C(CDCl_3)$ 20.9 (s, Me), 48.3 (d, J_{PC} 137, C–P), 53.5 (×2) (d, J_{PC} 7, POMe), 125.7 (d, J_{PC} 7, q), 126.4 (d, J_{PC} 3, CH), 126.6 (d, J_{PC} 3, CH), 127.0 (d, J_{PC} 4, CH), 127.5 (d, J_{PC} 4, CH), 127.7 (d, J_{PC} 4, CH), 129.0 (d, J_{PC} 6, q), 130.4 (d, J_{PC} 6, CH), 130.6 (d, J_{PC} 6, CH), 132.2 (d, J_{PC} 6, q), 132.6 (d, J_{PC} 6, q) and 137.7 (d, J_{PC} 4, q).

Dimethyl 2-(4′-methylphenylsulfanyl)benzylphosphonate 25 (X = S, R = Me). This compound, later shown to arise from the decomposition of the ylide **4** (R = 4-MeC_6H_4S), was isolated as a colourless oil, M^+, 322; $\delta_P(CDCl_3)$ 29.0; δ_H(270 MHz; $CDCl_3$) 2.31 (3 H, s, Me), 3.50 (2 H, d, J_{PH} 22, α-CH_2), 3.69 (6 H, d, J_{PH} 11, POMe), 7.10 (2 H, m, J_{PH} 8, 3′-H, 5′-H), 7.14 (2 H, m, J_{HH} 8, 2′-H, 6′-H), 7.14–7.29 (3 H, m, 3-H, 4-H, 5-H) and 7.46 (1 H, dm, J_{HH} 7.5, 6-H); $\delta_C(CDCl_3)$ 21.0 (s, Me), 30.6 (d, J_{PC} 139, α-CH_2), 52.9 (×2) (d, J_{PC} 7, POMe), 127.7 (d, J_{PC} 4, C-3), 128.0 (d, J_{PC} 4, C-5), 130.0 (×2) (s, C-2′, C-6′), 130.6 (×2) (s, C-3′, C-5′), 131.0 (d, J_{PC} 6, C-6), 132.4 (s, C-1′), 132.8 (d, J_{PC} 10, C-1), 133.3 (d, J_{PC} 3, C-4), 135.7 (d, J_{PC} 8, C-2) and 136.9 (s, C-4′).

5-Methyl-2-(4′-methylsulfanylphenyl)benzoic acid

To a solution of 2-iodo-5-methylbenzoic acid[10] (0.5 g, 1.9 mmol) and toluene-*p*-thiol (0.24 g, 1.9 mmol) in toluene (30 cm^3) in a round-bottom flask equipped with a Dean-Stark trap and condenser was added potassium hydroxide (0.43 g, 7.6 mmol) dissolved in the minimum of water. The mixture was then heated under reflux to remove any water from the reaction mixture after which the bulk of the toluene was removed by distillation and replaced with dimethylformamide (70 cm^3). The residual toluene was then removed by distillation and the resulting solution cooled to 100 °C. Cuprous oxide (30 mg, 0.16 mmol) was added to the mixture which was then heated under reflux with vigorous stirring for 16 h. After this it was allowed to cool and then poured onto ice. Concentrated hydrochloric acid was added to ensure that the solution was acidic and this was then extracted with chloroform (3 × 50 cm^3). The combined extracts were dried ($MgSO_4$), filtered, and evaporated under reduced pressure (20 mmHg, at 50 °C) to give the title acid (0.4 g, 81%) as a brown solid. This was purified by recrystallisation from aqueous ethanol to give a white solid, mp 158–160 °C (Found: C, 69.6; H, 5.4. $C_{15}H_{14}O_2S$ requires C, 69.75; H, 5.47%); δ_H(270 MHz; $CDCl_3$) 2.30 (3 H, s, Me), 2.40 (3 H, s, Me), 6.70 (1 H, d, J_{HH} 8, 3-H), 7.09 (1 H, dd, J_{HH} 8 and 2, 4-H), 7.24 (2 H, d, J_{HH} 8, 2′-H, 6′-H), 7.45 (2 H, d, J_{HH} 8, 3′-H, 5′-H), 7.94 (1 H, d, J_{HH} 8, 6-H) and 11.2 (br s, OH); $\delta_C(CDCl_3)$ 20.5 (Me), 21.3 (Me), 125.3 (q), 127.4 (CH), 129.0 (q), 130.6 (×2) (CH), 132.5 (CH), 134.07 (q), 134.14 (CH), 135.7 (×2) (CH), 139.3 (q), 141.4 (q) and 171.9 (C=O).

Preparation of dimethyl 5-methyl-2-(4′-methylphenylsulfanyl)-benzoylphosphonate 11 (X = S, R′ = R″ = Me) *in situ* and its reaction with trimethyl phosphite to give dimethyl 2,6-dimethyl-9*H*-thioxanthen-9-ylphosphonate 15 (X = S, R′ = R″ = Me)

5-Methyl-2-(4′-methylphenylsulfanyl)benzoic acid (0.25 g, 0.97 mmol) was mixed with thionyl chloride (5 cm^3) and toluene (1 cm^3) and the mixture stirred overnight under nitrogen. After this, all the volatile components were removed from the mixture by heating it under reduced pressure (20 mmHg at 60 °C). To the resulting residue, under nitrogen, was added trimethyl phosphite (0.36 g, 2.9 mmol) in dry toluene (8 cm^3) and the resulting mixture was heated at 100 °C for 20 h. Analysis of the reaction mixture by NMR spectroscopy indicated initial formation of the dimethyl 5-methyl-2-(4′-methylphenylsulfanyl)benzoylphosphonate (δ_P 1.0) which then reacted further to give several products. ^1H and ^{31}P NMR spectroscopy confirmed the presence of a thioxanthenylphosphonate [δ_P 24.7; δ_H 4.63 (1 H, d, J_{PH} 28, α-CH)] in the product. A sample of this component was isolated from the reaction mixture by chromatography on silica using ethyl acetate–light petroleum mixtures as eluents, followed by reverse phase HPLC using a Dynamax C-18 column with aqueous methanol (70%) as the eluent. Analysis of the NMR spectra of this component confirmed it to be dimethyl 2,6-dimethyl-9*H*-thioxanthen-9-ylphosphonate, M^+, 334.0789; $\delta_P(CDCl_3)$ 24.7; δ_H(270 MHz; $CDCl_3$) 2.31 (3 H, d, J_{PH} 2, Me), 2.33 (3 H, br s, Me), 3.54 (3 H, d, J_{PH} 11, POMe), 3.55 (3 H, d, J_{PH} 11, POMe), 4.63 (1 H, d, J_{PH} 28, 9-H), 7.02 (1 H, dm, J_{HH} 8, 3-H), 7.05 (1 H, dm, J_{HH} 8, 7-H), 7.15–7.19 (2 H, m, 1-H, 5-H), 7.22 (1 H, dd, J_{HH} 8, J_{PH} 3, 8-H) and 7.24 (1 H, d, J_{HH} 8, 4-H); $\delta_C(CDCl_3)$ 21.0 (×2) (s, Me), 48.4 (d, J_{PC} 137, C–P), 53.45 (d, J_{PC} 7, POMe), 53.55 (d, J_{PC} 7, POMe), 125.9 (d, J_{PC} 7, q), 126.5 (d, J_{PC} 4, CH), 127.0 (d, J_{PC} 3, CH), 127.4 (d, J_{PC} 3, CH), 128.7 (d, J_{PC} 5, CH), 129.0 (d, J_{PC} 7, q), 129.1 (d, J_{PC} 7, q), 130.4 (d, J_{PC} 5, CH), 131.3 (d, J_{PC} 6, CH), 132.6 (d, J_{PC} 6, q), 136.3 (d, J_{PC} 4, q) and 137.6 (d, J_{PC} 4, q).

2-(Phenoxymethyl)benzoic acid

A solution of methyl 2-bromomethylbenzoate (9.1 g, 39 mmol) in acetonitrile (20 cm^3) was added slowly to a solution of sodium phenoxide (4.6 g, 48 mmol) in acetonitrile (180 cm^3) and the mixture then heated under reflux for 3 h. After this it was evaporated under reduced pressure and the resulting residue dissolved in water (100 cm^3). After being adjusted to pH *ca.* 10 with sodium hydroxide the aqueous solution was extracted with ether (2 × 50 cm^3). The combined extracts were dried ($MgSO_4$), filtered and evaporated under reduced pressure (40 °C at 20 mmHg) to give methyl 2-(phenoxymethyl)benzoate (8.3 g, 85%) as a pale yellow oil which solidified with time (mp 55 °C). This ester (8.0 g) was hydrolysed with sodium hydroxide in aqueous methanol to give 2-(phenoxymethyl)benzoic acid (6.48 g, 86%) as a white solid, mp 127 °C (lit.,[11] mp 126–127 °C) M^+, 228 (Found: C, 73.45; H, 5.3. Calc. for $C_{14}H_{12}O_3$: C, 73.66; H, 5.30%); δ_H(270 MHz; $CDCl_3$) 5.56 (2 H, s, CH_2), 6.93–7.07 (3 H, m, 2′-H, 6′-H, 4′-H), 7.30 (2 H, m, 3′-H, 5′-H), 7.41 (1 H, t, J_{HH} 8, 5-H), 7.60 (1 H, td, J_{HH} 8 and 1, 4-H), 7.82 (1 H, d, J_{HH} 8, 3-H), 8.18 (1 H, dd, J_{HH} 8 and 1, 6-H) and 10.7 (1 H, br s, OH); $\delta_C(CDCl_3)$ 68.1 (CH_2), 114.9 (×2) (C-2′, C-6′), 121.0 (C-4′), 126.3 (C-1), 127.3 (×2) (C-5, C-6), 129.5 (×2) (C-3′, C-5′), 131.8 (C-3), 133.7 (C-4), 140.8 (C-2), 158.6 (C-1′) and 172.7 (C=O).

Dimethyl 2-(phenoxymethyl)benzoylphosphonate 1 (R = PhOCH$_2$)

To a solution of 2-(phenoxymethyl)benzoic acid (2.0 g, 8.7 mmol) in toluene (5 cm^3) was added thionyl chloride (10 cm^3) and the mixture stirred overnight at room temperature under nitrogen. The volatile components were then removed under reduced pressure (60 °C at 20 mmHg) from the mixture to give the crude 2-phenoxymethylbenzoyl chloride. To this material in toluene (5 cm^3) was added trimethyl phosphite (1.0 g, 8 mmol) and the mixture stirred for 17 h at room temperature under nitrogen. The volatile components were then removed under reduced pressure and the residue distilled *in vacuo* (0.05 mmHg at 130 °C) to give the phosphonate **1** (R = $PhOCH_2$) as a pale yellow oil, M^+, 306; $\delta_P(CDCl_3)$ 0.7; δ_H(270 MHz; $CDCl_3$) 3.91 (6 H, d, J_{PH} 11, POMe), 5.38 (2 H, s, CH_2), 6.92–7.02 (3 H, m, 2′-H, 4′-H, 6′-H), 7.25–7.31 (2 H, m, 3′-H, 5′-H), 7.48 (1 H, tm, J_{HH} 7.5, 5-H), 7.63 (1 H, td, J_{HH} 7.5 and 1, 4-H), 7.86 (1 H, dm, J_{HH} 7.5, 3-H) and 8.56 (1 H, dd, J_{HH} 7.5 and 1, 6-H); $\delta_C(CDCl_3)$ 54.2 (×2) (d, J_{PC} 7, POMe), 67.8 (s, CH_2), 114.8 (s, C-2′, C-6′), 121.1 (s, C-4′), 127.6 (s, C-5), 127.7 (d, J_{PC} 3, C-6), 129.5 (×2) (s, C-3′, C-5′), 132.9 (br s, C-3), 132.9 (d, J_{PC} 65, C-1), 134.2 (s, C-4), 139.8 (d, J_{PC} 10, C-2), 158.4 (s, C-1′) and 200.7 (d, J_{PC} 173, C=O).

Reaction of dimethyl 2-(phenoxymethyl)benzoylphosphonate with trimethyl phosphite

Dimethyl 2-(phenoxymethyl)benzoylphosphonate was prepared *in situ* by adding 2-(phenoxymethyl)benzoyl chloride

(0.54 g, 2.2 mmol) to trimethyl phosphite (0.82 g, 6.54 mmol) under nitrogen. This mixture was then heated at 100 °C for 2 h. ^{31}P NMR spectroscopy was used to monitor the progress of the reaction and this indicated the initial formation of the benzoylphosphonate **1** (R = $PhOCH_2$) (δ_P 0.7) which then reacted further to give the ylidic phosphonate **4** (R = $PhOCH_2$) (59%) and a mono-phosphonate product later identified as **28** (δ_P 24.5) (14%). Some of the phosphate **7** (R = $PhOCH_2$) was also present. The reaction mixture was heated under reduced pressure (85 °C at 0.01 mmHg) to remove the volatile components and the residue was subjected to reverse phase HPLC using a Dynamax C-18 column with aqueous methanol (70%) as the eluent to give the following compounds.

{(Dimethoxyphosphinoyl)[2-(phenoxymethyl)phenyl]-methyl} dimethyl phosphate 7 (R = $PhOCH_2$). This compound was isolated as a white solid, mp 158 °C, M^+, 430 (Found: C, 50.5; H, 5.95. $C_{18}H_{24}O_8P_2$ requires C, 50.22; H, 5.62%); $\delta_P(CDCl_3)$ 1.9 [d, J_{PP} 34, P(O)$(OMe)_2$] and 19.6 [d, J_{PP} 34, OP(O)$(OMe)_2$]; δ_H(270 MHz; $CDCl_3$) 3.51 (3 H, d, J_{PH} 11.5, MeOP), 3.63 (3 H, d, J_{PH} 10.5, MeOP), 3.70 (3 H, d, J_{PH} 11.5, MeOP), 3.77 (3 H, d, J_{PH} 10.5, MeOP), 5.21–5.32 (2 H, AB, J_{HH} 12, CH_2), 6.01 (1 H, dd, J_{PH} 14 and 11, α-CH), 6.96 (1 H, tm, J_{HH} 7, 4′-H), 7.03 (2 H, dm, J_{HH} 8, 2′-H, 6′-H), 7.25–7.32 (2 H, m, 3′-H, 5′-H), 7.32–7.48 (2 H, m, 4-H, 5-H), 7.49 (1 H, dm, J_{HH} 7, 3-H) and 7.79 (1 H, dm, J_{PH} 7, 6-H); $\delta_C(CDCl_3)$ 53.9 (d, J_{PC} 7, MeOP), 54.1 (d, J_{PC} 7, MeOP), 54.3 (d, J_{PC} 6, MeOP), 54.5 (d, J_{PC} 6, MeOP), 67.7 (s, CH_2), 70.4 (dd, J_{PC} 172 and 7, αCH), 114.9 (× 2) (s, C-2′, C-6′), 121.1 (s, C-4′), 128.5 (d, J_{PC} 2, CH), 129.0 (d, J_{PC} 5, CH), 129.1 (d, J_{PC} 2, CH), 129.4 (d, J_{PC} 2, C-4), 129.5 (× 2) (s, C-3′, C-5′), 132.1 (s, C-1), 135.3 (d, J_{PC} 7, C-2) and 158.4 (s, C-1′).

Tetramethyl [2-(phenoxymethyl)phenyl]methane-1,1-diphosphonate 6 (R = $PhOCH_2$). The ylidic phosphonate **4** (R = $PhOCH_2$) {δ_P 29.4 [d, J_{PP} 96, P(O)$(OMe)_2$] and 49.7 [d, J_{PP} 96, P$(OMe)_3$]} was isolated as its decomposition product, the bisphosphonate **6** (R = $PhOCH_2$) as a colourless oil, M^+, 414.0999; $\delta_P(CDCl_3)$ 21.6; δ_H(270 MHz; $CDCl_3$) 3.64 (6 H, d, J_{PH} 11, POMe), 3.76 (6 H, d, J_{PH} 11, POMe), 4.36 (1 H, t, J_{PH} 26, αCH), 5.10 (2 H, s, CH_2), 6.97 (2 H, dm, J_{HH} 8, 2′-H, 6′-H), 7.01 (1 H, m, 4′-H), 7.26 (2 H, m, 3′-H, 5′-H), 7.27–7.46 (3 H, m, 3-H, 4-H, 5-H) and 7.96 (1 H, m, 6-H); $\delta_C(CDCl_3)$ 39.5 (t, J_{PC} 133, αC), 53.7 (m, POMe), 54.1 (m, POMe), 68.7 (s, CH_2), 114.8 (× 2) (s, C-2′, C-6′), 121.3 (s, C-4′), 128.1 (t, J_{PC} 3, C-3), 128.7 (t, J_{PC} 2, C-5), 128.9 (t, J_{PC} 8, C-1), 129.6 (× 2) (s, C-3′, C-5′), 130.3 (br s, C-4), 131.1 (t, J_{PC} 4, C-6), 135.5 (t, J_{PC} 8, C-2) and 158.3 (s, C-1′).

11a-Dimethoxyphosphinoyl-5*H*-cyclohepta[*c*][2]benzopyran 27. This compound was isolated as a colourless oil which solidified with time to give a waxy solid, M^+, 304 (Found: C, 63.4; H, 5.3. $C_{16}H_{17}O_4P$ requires C, 63.14; H, 5.63%); $\delta_P(CDCl_3)$ 24.5; δ_H(270 MHz; $CDCl_3$) 3.79 (3 H, d, J_{PH} 10.5, POMe), 3.85 (3 H, d, J_{PH} 10.5, POMe), 4.87 (1 H, d, J_{HH} 13, 5-H), 5.29 (1 H, dd, J_{HH} 13, J_{PH} 2, 5-H), 5.38 (1 H, m, J_{PH} 10, 7-H), 6.20 (1 H, m, 11-H), 6.36–6.42 (3 H, m, 8-H, 9-H, 10-H), 7.13 (1 H, d, J_{HH} 7, 4-H), 7.31 (1 H, tm, J_{HH} 7.5, 3-H), 7.43 (1 H, t, J_{HH} 7, 2-H) and 7.87 (1 H, dd, J_{HH} 8, J_{PH} 3, 1-H); $\delta_C(CDCl_3)$ 51.0 (d, J_{PC} 151, C–P), 53.76 (d, J_{PC} 8, POMe), 53.79 (d, J_{PC} 8, POMe), 68.8 (s, CH_2), 108.0 (d, J_{PC} 6, CH), 119.8 (d, J_{PC} 5, CH), 124.4 (d, J_{PC} 3, CH), 125.1 (s, CH), 127.5 (d, J_{PC} 4, CH), 127.6 (s, CH), 127.9 (d, J_{PC} 4, CH), 128.9 (d, J_{PC} 6, CH), 129.8 (d, J_{PC} 5, CH), 133.9 (d, J_{PC} 8, q), 135.1 (d, J_{PC} 5, q) and 141.3 (s, q).

Dimethyl 2-(phenoxymethyl)benzylphosphonate 25 (X = CH_2O, R = H). This compound, later shown to arise from the decomposition of the ylide **4** (R = $PhOCH_2$), was isolated as a colourless oil, M^+, 306 (Found: C, 62.5; H, 6.35. $C_{16}H_{19}O_4P$ requires C, 62.74; H, 6.25%); $\delta_P(CDCl_3)$ 29.3; δ_H(270 MHz; $CDCl_3$) 3.32 (2 H, d, J_{PH} 22, α-CH_2), 3.65 (6 H, d, J_{PH} 10.5, POMe), 5.18 (2 H, s, CH_2), 6.97 (1 H, t, J_{HH} 7, 4′-H), 7.00 (2 H, d, J_{HH} 8, 2′-H, 6′-H), 7.26–7.39 (5 H, m, 3′-H, 5′-H, 3-H, 4-H, 5-H) and 7.44 (1 H, m, 6-H); $\delta_C(CDCl_3)$ 29.6 (d, J_{PC} 139, α-C), 59.9 (× 2) (d, J 7, POMe), 68.3 (s, CH_2O), 114.8 (× 2) (s, C-3′, C-5′), 121.1 (s, C-4′), 127.5 (d, J_{PC} 3, CH), 128.5 (d, J_{PC} 3, CH), 129.5 (× 2) (s, C-2′, C-6′), 129.7 (d, J_{PC} 4, CH), 130.2 (d, J_{PC} 9, q), 131.2 (d, J_{PC} 6, CH), 135.6 (d, J_{PC} 7, q) and 158.7 (s, C-1′).

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