Reactions of carbene intermediates from the reaction of trialkyl phosphites with dialkyl benzoylphosphonates: preparation and reactions of dimethyl 2-(*N*-*tert*-butyl-*N*-methylamino)benzoylphosphonate and dimethyl 2-(methylamino)benzoylphosphonate

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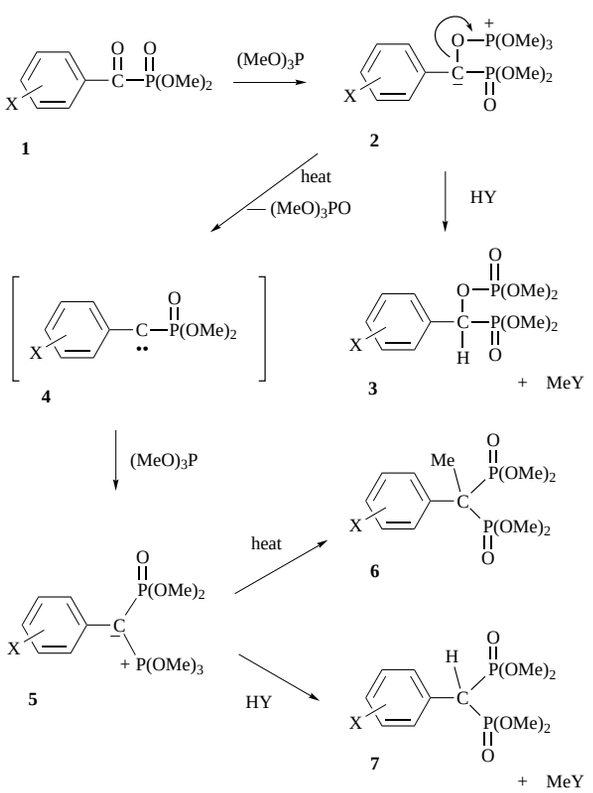
Dimethyl 2-(methylamino)benzoylphosphonate has been prepared by the thermal decomposition of dimethyl 2-(*N*-*tert*-butyl-*N*-methylamino)benzoylphosphonate formed by the action of triethylamine on 1-*tert*-butyl-3-(dimethoxyphosphinyl)-1-methyl-2,1-benzisoxazolinium hexafluorophosphate. The reactions of both benzoylphosphonates with trimethyl phosphite proceed *via* carbene intermediates 4 to initially give ylidic phosphonates 5, which for 5 (X = 2-MeNH) undergoes cyclisation and rearrangement to give the novel 2-oxophosphorindoline 11.†

We have previously shown that dialkyl benzoylphosphonates **1** react with trialkyl phosphites to give anionic intermediates **2**, which in the presence of proton donors are usually trapped to give the phosphates **3**, although other products have been observed (Scheme 1).[1] We have also shown that if no electrophiles are present to trap the intermediates **2**, cleavage of the α-C–O bond can occur to give carbene intermediates **4**.[2] If a suitable substituent is present at the 2-position on the benzene ring this can react with the carbene centre to give cyclic products[2–5] but if this is unfavourable the carbenes **4** will be preferentially trapped by the trialkyl phosphite in the reaction mixture to give ylidic phosphonates **5.**

Dialkyl benzoylphosphonates are invariably prepared by the reaction of a trialkyl phosphite with the appropriate carboxylic acid chloride which in turn is usually generated by the action of thionyl chloride on the carboxylic acid. While this approach has proved suitable for the preparation of a wide range of substituted dialkyl benzoylphosphonates, difficulties arise with the preparation of those benzoylphosphonates possessing basic substituents such as amino groups. In our experience, efforts to prepare amino-substituted benzoyl chlorides invariably lead to the formation of their hydrochloride salts and the presence of this additional hydrogen chloride can then act as a proton donor when attempts are made to prepare the corresponding benzoylphosphonates resulting in the formation of the phosphates **3** rather than the benzoylphosphonates **1**. Moreover, reagents such as triphenylphosphine in carbon tetrachloride[6] which can convert carboxylic acids to the corresponding acid chlorides under essentially neutral conditions are not easily employed in the case of amino-substituted benzoic acids which are not readily soluble in the organic solvents usually used. The reported preparation of a phosphonate believed to be dimethyl 2-(*N*-*tert*-butyl-*N*-methylamino)benzoylphosphonate **1** (X = 2-Bu^{t}MeN)[7] by the reaction of the perchlorate salt **9** (Z = ClO_4) with an organic base was therefore of particular interest to us in this context and worthy of further investigation.

† IUPAC name for phosphorindoline: 2,3-dihydro-1*H*-1,2-benzazaphosphole.

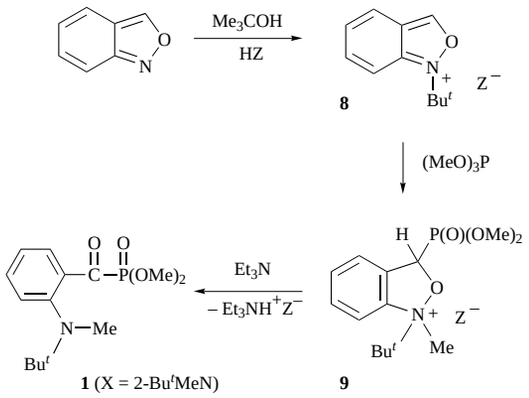


Scheme 1

Results and discussion

As previously reported[8] reaction of anthranil‡ with 2-methylpropan-2-ol in the presence of perchloric acid led to the formation of the anthranilium salt **8** (Z = ClO_4) which on reaction with trimethyl phosphite gave the anthranilium salt **9** (Z = ClO_4) (Scheme 2). Treatment of this material with triethyl-

‡ 2,1-Benzisoxazole.



Scheme 2

amine gave a moisture sensitive product which readily hydrolysed to 2-(*N*-*tert*-butyl-*N*-methylamino)benzoic acid. The product also reacted with methanol to give methyl 2-(*tert*-butylmethylamino)benzoate and dimethyl phosphite and it was on this basis that previous workers[7] had proposed the involvement of dimethyl 2-(*N*-*tert*-butyl-*N*-methylamino)benzoylphosphonate **1** (X = 2-Bu^{t}MeN). By carefully excluding water from the reaction we were able to isolate the benzoylphosphonate **1** (X = 2-Bu^{t}MeN) in a reasonably good state of purity and to confirm its structure by NMR spectroscopy. In particular, the product gave a signal in the ^{31}P NMR spectrum around 0 ppm, (δ_P −1.6), typical of benzoylphosphonates, and a characteristically large doublet in the carbonyl region of the ^{13}C NMR spectrum [δ_C 206.0 (d, J_{PC} 185 Hz)]. An initial attempt to purify the crude benzoylphosphonate **1** (X = 2-Bu^{t}MeN) by distillation appeared successful although subsequent analysis indicated that the *tert*-butyl group had been lost from the nitrogen during the distillation to give the benzoylphosphonate **1** (X = 2-MeNH). However, more seriously, a subsequent attempt to distil some crude benzoylphosphonate **1** (X = 2-Bu^{t}MeN) resulted in an explosion, probably due to the presence of perchlorate salts in the distillation residue. For this reason, efforts were made to find an alternative route to the benzoylphosphonate **1** (X = 2-Bu^{t}MeN) avoiding the use of perchloric acid.

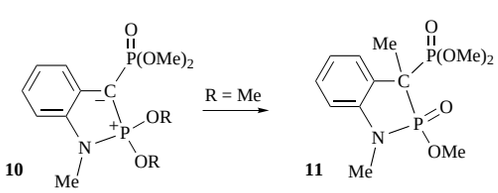
The reaction of anthranil with 2-methylpropan-2-ol in the presence of a variety of acids, including sulfuric, methanesulfonic, trifluoromethanesulfonic and toluene-4-sulfonic acid, was investigated but, while results initially looked encouraging, attempts to precipitate the anticipated anthranilium salts **8** resulted in the formation of oils highly contaminated with the acids used in their preparation and therefore unsuitable for subsequent reaction with trimethyl phosphite. In contrast, the use of hexafluorophosphoric acid resulted in the formation of the anthranilium salt **8** (Z = PF_6) which precipitated from the crude reaction mixture in good yield on the addition of diethyl ether. This salt was then converted into the benzoylphosphonate **1** (X = 2-Bu^{t}MeN) *via* the anthranilium salt **9** (Z = PF_6) in an analogous manner to that used for the corresponding perchlorate salt. Attempts to distil the benzoylphosphonate **1** (X = 2-Bu^{t}MeN), formed in this way, confirmed our earlier observation that the *tert*-butyl group was readily lost from the nitrogen under these conditions to give **1** (X = 2-MeNH) and that it was difficult to avoid such decomposition even when great care was taken during the distillation. Subsequent reactions of the benzoylphosphonate **1** (X = 2-Bu^{t}MeN) were therefore carried out on this material prior to distillation.

The reaction of the benzoylphosphonate **1** (X = 2-Bu^{t}MeN) with trimethyl phosphite proceeded as anticipated, with the involvement of the carbene intermediate **4** (X = 2-Bu^{t}MeN) being indicated by the formation of trimethyl phosphite and the isolation of the bisphosphonate **7** (X = 2-Bu^{t}MeN) in reasonable yield from the reaction mixture. A particularly unusual feature of this bisphosphonate is that its ^{31}P NMR spectrum shows two doublets [δ_P 22.8 (d, J_{PP} 6 Hz) and 23.3 (d, J_{PP} 6 Hz)] rather than the expected singlet. This clearly indicated that the two phosphorus atoms in this bisphosphonate are non-equivalent on the NMR timescale and suggests that the bulky *ortho* substituent on the benzene ring is restricting rotation about the bond between the α-carbon and the benzene ring. Preliminary modelling studies provide additional support for this view.[9] However, warming the NMR sample to 80 °C produced no significant broadening of the phosphorus resonances.

The steric effects of the *o*-(*N*-*tert*-butyl-*N*-methylamino) substituent can also be seen in the ^{1}H NMR spectrum of the benzoylphosphonate **1** (X = 2-Bu^{t}MeN) which clearly indicates that the carbonyl group is twisted out of the plane of the benzene ring leading, among other things, to a marked upfield shift of the 6-H resonance relative to its position in the benzoylphosphonate **1** (X = 2-MeNH).

The reaction of trimethyl phosphite with the benzoylphosphonate **1** (X = 2-MeNH) was also investigated to see if the N−H proton would act as a proton donor and trap the initially formed anionic intermediate **2** (X = 2-MeNH) to give a phosphate such as **3** (X = 2-Me_2N). However, no evidence for such a reaction was observed. Instead the reaction proceeded cleanly to initially give an ylidic phosphonate [δ_P 69.0 (d, J_{PP} 73 Hz) and 25.9 (d, J_{PP} 73 Hz)] and trimethyl phosphate. This clearly indicates that the carbanionic centre in **2** (X = 2-MeNH) is not sufficiently basic to abstract the adjacent N−H proton, and that this is also true for the carbanionic centre in the ylides subsequently formed. It should be noted, however, that the ^{31}P NMR shifts of the ylidic phosphonate from **1** (X = 2-MeNH) are significantly different from those expected for **5** (X = 2-MeNH) based on those systems studied so far [δ_P *ca.* 54 and *ca.* 31].[2] This suggests that the ylide **5** (X = 2-MeNH), which would result from trapping the carbene **4** (X = 2-MeNH) with trimethyl phosphite, undergoes rapid cyclisation to give the ylidic phosphonate **10** (R = Me). While it could be argued on electronegativity grounds that the replacement of an oxygen substituent on the phosphonium centre by a nitrogen one would produce an upfield rather than a downfield shift, there is clear evidence that steric factors are also important and that amino substituents with two carbons β to the phosphonium centre produce an overall downfield shift.[10] The effect of ring formation is more difficult to predict in this particular case but it appears to further increase the chemical shift of the phosphonium centre.

As the reaction between trimethyl phosphite and the benzoylphosphonate **1** (X = 2-MeNH) proceeded, the initially observed ylide **10** (R = Me) underwent a rearrangement to give one major isomer of the diphosphorus compound **11** (Scheme 3). Strong evidence for the presence of the P−N bond in the



Scheme 3

isomers of **11** is provided by ^{1}H NMR spectroscopy which shows coupling between the *N*-methyl group and only one of the phosphorus atoms in both isomers. This rearrangement of **10** (R = Me) is analogous to the observed formation of the bisphosphonates **6** on heating the ylidic phosphonates **5**[2] and provides further support for the structure of the precursor of **11** as being the ylidic phosphonate **10** (R = Me). It is interesting to note that no coupling (J_{PP} < 2 Hz) was observed between the resonances of the two phosphorus atoms in the major isomer of **11** despite their close proximity. As with the rearrangements

of the ylidic phosphonates **5** previously studied,[2] the reaction of the benzoylphosphonate **1** (X = 2-MeNH) with triethyl phosphite led to the formation of the ylidic phosphonate **10** (R = Et) which proved to be resistant to further thermal rearrangement.

In conclusion, we have shown that the reaction of triethylamine with the anthranilium salt **9** ($Z = PF_6$) provides an unusual route to two 2-amino-substituted dialkyl benzoylphosphonates and that both these phosphonates react with trialkyl phosphites to give compounds which possess novel features. The preparation of other amine-containing benzoylphosphonates is being investigated.

Experimental

NMR spectra were obtained on JEOL EX270 spectrometers. *J* Values are given in Hz. In the assignment of ^{13}C NMR spectra, Q refers to quaternary carbon.

1-*tert*-Butyl-3-(dimethoxyphosphinoyl)-1-methyl-2,1-benzisoxazolinium perchlorate 9 (Z = ClO_4)

This material was prepared by a modification of the method of Olofson *et al.*[7] A mixture of 1-*tert*-butyl-2,1-benzisoxazolinium perchlorate **8** ($Z = ClO_4$)[8] (23 g, 0.084 mol) and trimethyl phosphite (15.6 g, 0.126 mol) in acetonitrile (150 cm^3) was stirred at room temperature for several hours and the resulting yellow solution then poured into diethyl ether (400 cm^3). The resulting gum was triturated with diethyl ether to leave a solid residue which was recrystallised from acetone–diethyl ether (50:50) to give 1-*tert*-butyl-1-methyl-3-(dimethoxyphosphinoyl)-2,1-benzisoxazolinium perchlorate as a white solid (28.4 g, 84.7%), mp 113 °C (lit.,[7] 114 °C decomp.); δ_P 14.7.

1-*tert*-Butyl-2,1-benzisoxazolinium hexafluorophosphate 8 (Z = PF_6)

Hexafluorophosphoric acid (22.54 g, 0.27 mol) was added slowly to a stirred mixture of anthranil (2,1-benzisoxazole) (5.0 g, 42 mmol) and 2-methylpropan-2-ol (3.1 g, 42 mmol) at 0 °C in a Teflon beaker, and the resulting solution was then stirred overnight at room temperature. After the addition of a little acetone (*ca*. 5 ml), diethyl ether was added to precipitate the anthranilium salt. This solid was filtered off and recrystallised from acetone–diethyl ether (1:2) and then dried under vacuum to give the title compound **8** as a pale yellow solid (10.1 g, 75%), mp 143–145 °C (decomp.); *m/z* 176 [$M - (PF_6)^+$] (Found: C, 41.1; H, 4.5; N, 4.2. $C_{11}H_{14}NOPF_6$ requires C, 41.11; H, 4.39; N, 4.36%); δ_H([$^2H_6$]acetone; 270 MHz) 2.04 (9H, s, CMe_3), 7.62–7.69 (1H, ddd, J_{HH} 9.0, 6 and 1), 8.13–8.30 (3H, m), 10.24 (1H, s, 3-H); δ_C($CDCl_3$) 28.4 (Me), 71.5 (Q), 112.1 (CH), 121.9 (Q), 124.5 (CH), 128.5 (CH), 141.9 (CH), 146.5 (Q), 161.8 (CH).

1-*tert*-Butyl-3-(dimethoxyphosphinoyl)-1-methyl-2,1-benzisoxazolinium hexafluorophosphate 9 (Z = PF_6)

A mixture of 1-*tert*-butyl-2,1-benzisoxazolinium hexafluorophosphate **8** ($Z = PF_6$) (5.00 g, 15.5 mmol) and trimethyl phosphite (1.92 g, 15.5 mmol) in acetonitrile (15 ml) was stirred overnight at room temperature in a glass vessel under an atmosphere of dry nitrogen. The resulting solution was then poured into diethyl ether to precipitate the product which was filtered off and recrystallised from acetone–diethyl ether (1:1). The title compound (5.9 g, 85%) was isolated as a pale yellow solid, mp 112–114 °C (decomp.); *m/z* 300 (M^+) (Found: C, 37.9; H, 5.4; N, 3.15. $C_{14}H_{23}NO_4P_2F_6$ requires C, 37.74; H, 5.21; N, 3.15%); δ_P([$^2H_6$]acetone) 13.5 (s, MeOP), −139.6 (septet, J_{PF} 707, PF_6); δ_H([$^2H_6$]acetone; 270 MHz) 1.67 (9H, s, CMe_3), 3.81 (3H, d, J_{PH} 11, MeOP), 3.93 (3H, d, J_{PH} 11, MeOP), 4.10 (3H, s, NMe), 6.55 (1H, s, 3-H), 7.75–7.92 (3H, m, 4-H, 5-H, 6-H), 8.03 (1H, br d, J_{HH} 8, 7-H); δ_C([$^2H_6$]acetone) 24.1 (s, Me_3), 53.1 (d, J_{PC} 2, NCH_3), 54.8 (d, J_{PC} 7, MeOP), 55.1 (d, J_{PC} 7, MeOP), 82.9 (d, J_{PC} 165, PCH), 86.4 (d, J_{PC} 3, $NCMe_3$), 119.7 (d, J_{PC} 2, CH), 125.1 (d, J_{PC} 3, CH), 130.8 (d, J_{PC} 4, Q), 131.9 (d, J_{PC} 2, CH), 133.8 (d, J_{PC} 2, CH), 139.8 (d, J_{PC} 7, Q).

Dimethyl 2-(*N*-*tert*-butyl-*N*-methylamino)benzoylphosphonate 1 (X = 2-Bu^{t}MeN)

1-*tert*-Butyl-3-(dimethoxyphosphinoyl)-1-methyl-2,1-benzisoxazolinium hexafluorophosphate **9** ($Z = PF_6$) (1.5 g, 3.4 mmol) was added dropwise to a cooled solution of triethylamine (0.6 g, 6.7 mmol) in dichloromethane (10 cm^3) at 0 °C, ensuring the reaction temperature did not rise above 5 °C. After a few minutes, the solvent was evaporated under reduced pressure (20 mmHg), and the residue extracted with diethyl ether (3 × 10 cm^3). The solvent was then removed from the extracts to give dimethyl 2-(*N*-*tert*-butyl-*N*-methylamino)benzoylphosphonate **1** (X = 2-Bu^{t}MeN) as a moisture sensitive yellow oil (0.9 g, 88%), δ_P($CDCl_3$) −1.6; δ_H($CDCl_3$; 270 MHz) 1.06 (9H, s, CMe), 2.84 (3H, s, NMe), 3.78 (3H, d, J_{PH} 11, POMe), 3.81 (3H, d, J_{PH} 11, POMe), 7.24 (1H, m, 5-H), 7.35 (2H, br d, J_{HH} 8, 3-H, 6-H), 7.55 (1H, m, 4-H); δ_H([$^2H_6$]acetone; 270 MHz) 1.06 (9H, s, CMe), 2.84 (3H, s, NMe), 3.76 (6H, d, J_{PH} 11, POMe), 7.34 (2H, m, 5-H, 6-H), 7.47 (1H, br d, J_{HH} 8, 3-H), 7.61 (1H, m, 4-H); δ_C($CDCl_3$) 26.5 (s, CMe_3), 37.4 (s, NCH_3), 53.8 (br d, J_{PC} 8, MeOP), 57.2 (s, $NCMe_3$), 125.5 (d, J_{PC} 1.5, C-3), 127.2 (s, C-5), 127.3 (d, J_{PC} 3, C-6), 132.7 (s, C-4), 139.6 (d, J_{PC} 56, C-1), 151.8 (s, C-2), 206.0 (d, J_{PC} 185, C=O).

The same product was obtained by the reaction of 1-*tert*-butyl-3-(dimethoxyphosphinoyl)-1-methyl-2,1-benzisoxazolinium perchlorate **9** ($Z = ClO_4^-$) with triethylamine using the procedure previously reported.[7]

Decomposition of the dimethyl 2-(*N*-*tert*-butyl-*N*-methylamino)benzoylphosphonate **1** (X = Bu^{t}MeN) in boiling methanol led to the formation of methyl 2-(*N*-*tert*-butyl-*N*-methylamino)benzoate as previously reported.[7]

Dimethyl 2-(*N*-methylamino)benzoylphosphonate 1 (X = 2-MeNH)

NB: See warning in discussion section about distillation of the benzoylphosphonate **1** (X = 2-Bu^{t}MeN) from 1-*tert*-butyl-3-(dimethoxyphosphinoyl)-1-methyl-2,1-benzisoxazolinium perchlorate **9** ($Z = ClO_4^-$). A quantity of crude dimethyl 2-(*N*-*tert*-butyl-*N*-methylamino)benzoylphosphonate **1** (X = 2-Bu^{t}MeN) (1 g), prepared as previously described, was heated in a distillation apparatus under reduced pressure (0.04 mmHg). Decomposition occurred and dimethyl 2-(*N*-methylamino)benzoylphosphonate **1** (X = 2-MeNH) (0.65 g, 79%) distilled over as a pale yellow oil, bp 148 °C at 0.04 mmHg; *m/z* 243 (M^+) (Found: C, 49.2; H, 6.0; N, 5.55. $C_{10}H_{14}NO_4P$ requires C, 49.37; H, 5.8; N, 5.76%) δ_P($CDCl_3$) 2.9; δ_H($CDCl_3$; 270 MHz) 2.96 (3H, s, NMe), 3.90 (6H, d, J_{PH} 11, POMe), 6.66–6.77 (2H, m, 3-H, 5-H), 7.46 (1H, ddd, J_{HH} 1.5, 7 and 9, 4-H), 8.43 (1H, dd, J_{HH} 1.5 and 8, 6-H); δ_C($CDCl_3$) 29.1 (s, NMe), 53.8 (d, J_{PC} 7, POMe), 111.2 (d, J_{PC} 5, C-3), 114.7 (s, C-5), 117.2 (d, J_{PC} 61, C-1), 134.5 (s, C-6), 136.7 (s, C-4), 152.9 (d, J_{PC} 14, C-2), 196.4 (d, J_{PC} 173, C=O).

Reaction of dimethyl 2-(*N*-*tert*-butyl-*N*-methylamino)benzoylphosphonate 1 (X = 2-Bu^{t}MeN) with trimethyl phosphite

The crude dimethyl 2-(*N*-*tert*-butyl-*N*-methylamino)benzoylphosphonate **1** (X = 2-Bu^{t}MeN) (2.0 g, 6.7 mmol), prepared as previously described, was heated with trimethyl phosphite (1.65 g, 13.3 mmol) at 105 °C under an atmosphere of dry nitrogen for 4 h. Volatile components were removed from the reaction mixture by heating for 1 h under reduced pressure (70 °C at 0.003 mmHg) and analysis of the residue by ^{31}P NMR spectroscopy indicated the major component present to be *tetramethyl* [2-(N-tert-*butyl*-N-*methylamino*)*phenyl*]*methane*-1,1-*diphosphonate* **7** (X = 2-Bu^{t}MeN). This material was isolated as a colourless oil by reversed-phase HPLC using aqueous methanol (70%) as the eluent; *m/z* (FAB) 394.1536 ($M + H^+$); δ_P 22.8 (d, J_{PP} 6), 23.3 (d, J_{PP} 6); δ_H($CDCl_3$; 270 MHz) 1.15 (9H, s, CMe_3),

2.61 (3H, s, NMe), 3.64 (3H, d, J_{PH} 11, MeOP), 3.66 (3H, d, J_{PH} 11, MeOP), 3.73 (3H, d, J_{PH} 11, MeOP), 3.84 (3H, d, J_{PH} 11, MeOP), 5.56 (1H, br t, J_{PH} 25, α-CH), 7.14–7.30 (2H, m, 4-H, 5-H), 7.39 (1H, br d, J_{PH} 11, 3-H), 7.82 (1H, m, 6-H); $\delta_C(CDCl_3)$ 27.8 (s, C*Me*$_3$), 37.71 (br s, NMe), 37.74 (dd, J_{PC} 134 and 137, α-CH), 53.15 (d, J_{PC} 7, POMe), 53.3 (d, J_{PC} 7, POMe), 53.8 (d, J_{PC} 7, POMe), 53.9 (d, J_{PC} 7, POMe), 55.3 (br s, *C*Me$_3$), 125.3 (t, J_{PC} 2.5, C-5), 128.0 (t, J_{PC} 3, C-3), 128.2 (t, J_{PC} 2, C-4), 129.6 (dd, J_{PC} 6 and 8, C-1), 130.3 (t, J_{PC} 4, C-6), 151.3 (t, J_{PC} 8, C-2).

Reaction of dimethyl 2-(*N*-methylamino)benzoylphosphonate 1 (X = 2-MeNH) with trimethyl phosphite

A mixture of dimethyl 2-(*N*-methylamino)benzoylphosphonate **1** (X = 2-MeNH) (2 g, 6.3 mmol) and trimethyl phosphite (1.6 g, 12.5 mmol) was heated at 105 °C in an atmosphere of dry nitrogen and the progress of the reaction monitored by ^{31}P NMR spectroscopy. This indicated the initial formation of trimethyl phosphate and the ylide **10** (R = Me) [δ_P 69.0 (d, J_{PP} 73) and 25.9 (d, J_{PP} 73)]. As the reaction proceeded the ylide **10** (R = Me) underwent a rearrangement to give essentially one isomer of the diphosphorus compound **11**. After 4 h the reaction was complete and the volatile components in the reaction mixture were removed by heating under reduced pressure (60 °C at 0.05 mmHg) for 1 h. An analytically pure sample of the major isomer of **11** was obtained using reversed-phase HPLC with aqueous methanol (60%) as eluent.

3-Dimethoxyphosphinyl-2-methoxy-1,3-dimethyl-2-oxo-2,3-dihydro-1*H*-1,2λ^5-benzazaphosphole 11. The major isomer of **11** was isolated as a yellow oil, *m*/*z* 319 (M^+) (Found: C, 45.58; H, 6.16; N, 4.39. $C_{12}H_{19}NO_5P_2$ requires C, 45.14; H, 5.96; N, 4.39%); $\delta_P(CDCl_3)$ 45.5 (s, NP), 26.3 [s, P(O)(OMe)$_2$]; $\delta_H(CDCl_3$; 270 MHz) 1.82 (3H, t, J_{PH} 16.5, CMe), 2.99 (3H, d, J_{PH} 8.5, NMe), 3.63 (3H, d, J_{PH} 11, POMe), 3.79 (3H, d, J_{PH} 11, POMe), 3.94 (3H, d, J_{PH} 11.5, POMe), 6.64 (1H, d, J_{HH} 7.5, 7-H), 6.92 (1H, t, J_{HH} 7.5, 5-H), 7.25 (1H, tm, J_{HH} 7.5, 6-H), 7.44 (1H, dm, J_{HH} 7.5, 4-H); $\delta_C(CDCl_3)$ 19.3 (t, J_{PC} 5, CMe), 27.1 (s, NMe), 40.4 (dd, J_{PC} 111 and 142, C-3), 53.7 (d, J_{PC} 7, POMe), 54.4 (d, J_{PC} 7, POMe), 55.0 (d, J_{PC} 6, POMe), 108.4 (t, J_{PC} 11, C-7), 120.5 (d, J_{PC} 1, C-5), 124.8 (t, J_{PC} 6, C-3a), 125.9 (dd, J_{PC} 4 and 12, C-4), 129.1 (br s, C-6), 143.4 (dd, J_{PC} 9 and 27, C-7a).

The minor isomer of **11** was isolated in an impure form containing some of the major isomer, $\delta_P(CDCl_3)$ 45.0 (d, J_{PP} 10, NP), 24.8 [d, J_{PP} 10, P(O)(OMe)$_2$]; $\delta_H(CDCl_3$; 270 MHz) 1.78 (3H, t, J_{PH} 16, CMe), 3.04 (3H, d, J_{PH} 9, NMe), 3.57 (3H, d, J_{PH} 11, POMe), 3.84 (3H, d, J_{PH} 11, POMe), 3.85 (3H, d, J_{PH} 11, POMe), 6.66 (1H, d, J_{HH} 7, 7-H), 6.95 (1H, t, J_{HH} 7.5, 5-H), 7.25 (1H, m, 6-H), 7.39 (1H, dm, J_{HH} 7.5, 4-H); $\delta_C(CDCl_3)$ 16.7 (t, J_{PC} 5, CMe), 27.3 (d, J_{PC} 1.5, NMe), 40.4 (dd, J_{PC} 115 and 137, C-3), 54.0 (d, J_{PC} 7, POMe), 54.2 (d, J_{PC} 6, POMe), 54.6 (d, J_{PC} 7, POMe), 108.4 (t, J_{PC} 11, C-7), 120.6 (d, J_{PC} 2, C-5), 124.3 (dd, J_{PC} 6 and 8.5, C-3a), 126.3 (dd, J_{PC} 4 and 12, C-4), 129.2 (d, J_{PC} 3, C-6), 143.4 (dd, J_{PC} 7 and 25, C-7a).

Reaction of dimethyl 2-(*N*-methylamino)benzoylphosphonate 1 (X = 2-MeNH) with triethyl phosphite

A mixture of dimethyl 2-(*N*-methylamino)benzoylphosphonate **1** (X = 2-MeNH) (2 g, 6.3 mmol) and triethyl phosphite (3.15 g, 19 mmol) was heated at 105 °C for 3 h in an atmosphere of dry nitrogen. Analysis of the reaction mixture by ^{31}P NMR spectroscopy indicated the formation of equimolar quantities of the ylidic phosphonate **10** (R = Et), $\delta_P(CDCl_3)$ 25.8 [d, J_{PP} 74, P(OMe)$_2$], 65.3 (d, J_{PP} 74, PN) and triethyl phosphate.

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