Tetrahedron Vol. 46, No. 20, pp. 7175-7196, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

Synthesis of Organophosphorus Compounds *via* Silyl Esters of Phosphorous Acids

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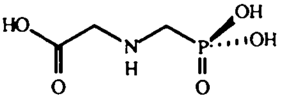
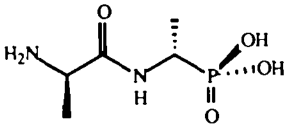
(*Received in UK* 25 *June* 1990)

ABSTRACT: The addition of trimethylsilyloxy phosphorus (III) derivatives, generated *in situ*, to imines at room temperature provides a mild, selective and high yielding route to α-aminoalkylphosphonate and α-aminoalkylphenylphosphinate esters. Isocyanates and carbodiimides react similarly to give phosphonoureas and phosphonoguanidines respectively; aldehydes and ketones are much less reactive, and cyanides are inert.

Introduction

In the past twenty years, considerable effort has been devoted to the synthesis and investigation of biological activity of α-aminophosphonic acids, largely because of their structural analogy with α-aminocarboxylic acids.[1] Several α-aminophosphonic acid derivatives such as the herbicide glyphosate (Roundup) and the antibacterial alafosfalin, are widely used commercially.

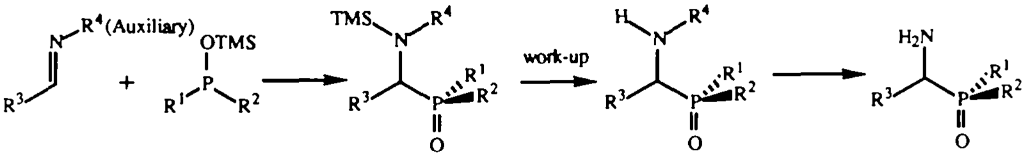

Glyphosate


Alafosfalin

The standard synthesis of α-aminophosphonic acids involves thermal addition of a trivalent phosphorus acid or ester to an imine, which itself may be generated *in situ* from the amine and aldehyde.[2] These thermal reactions are particularly useful for the large scale preparation of simple α-aminophosphonic acids,[3] but are less useful in multi-step synthesis of more complex and delicate compounds. Various modifications have been introduced in recent years with the aim of providing milder reaction conditions[4] but no systematic investigation of synthetically convenient routes to these compounds has been reported.

As part of a general investigation of the synthesis of bioactive compounds containing phosphorus, we sought a mild, selective synthetic route to α-aminophosphonic acids and esters which could accommodate a wide range of substituents on phosphorus and the α-carbon. Evans has shown that some trimethylsilyl esters of phosphorous acids react with aldehydes and ketones under relatively mild conditions.[5] Also a report of the addition reaction of bis(trimethylsilyl) phosphonite with imines has appeared recently.[6] The silylated phosphites are isolated only in modest yield and are hydrolytically sensitive, and we therefore opted for their *in situ* generation (*cf* reference 7) which provided a much more convenient and efficient route.

We have studied the scope and limitations of the addition of the phosphorus reagents to imines and related functional groups and report the effect of variation of the imine (R^3 and R^4) and phosphorus substituents (R^1 and R^2) (Scheme 1).

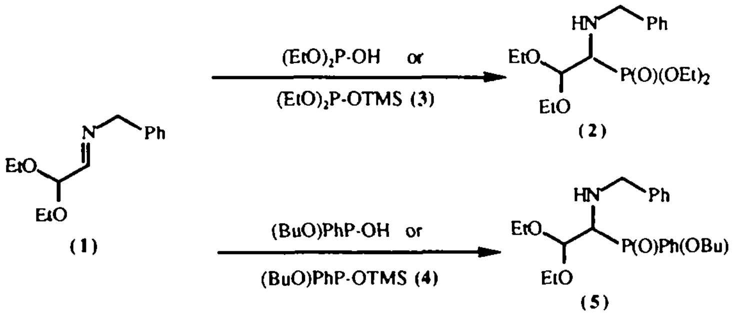


Scheme 1

Results and Discussion

All O-TMS esters were generated *in situ* with chlorotrimethylsilane and triethylamine in a chlorinated solvent (usually dichloromethane) at 0°C and the complete formation of the tri-coordinated phosphorus species was established by ^{31}P NMR (see Experimental). The imines were readily prepared by standard condensation of the appropriate aldehydes and amines.

The chlorotrimethylsilane mediated reactions all worked well under mild conditions (0°C to room temperature in dichloromethane, with aqueous work up), to give better yields and cleaner reactions than the neat uncatalysed, thermal reactions. Thus 2,2-diethoxyacetaldehyde N-benzylimine (**1**) and diethyl phosphite at 110°C gave the addition product (**2**) in 55% yield; the same imine with diethyl trimethylsilyl phosphite (**3**) gave 79%. Similarly *n*-butyl phenylphosphonite[8] and its trimethylsilylated derivative (**4**) reacted with the same imine to afford 43% and 81%, respectively, of the addition product (**5**).

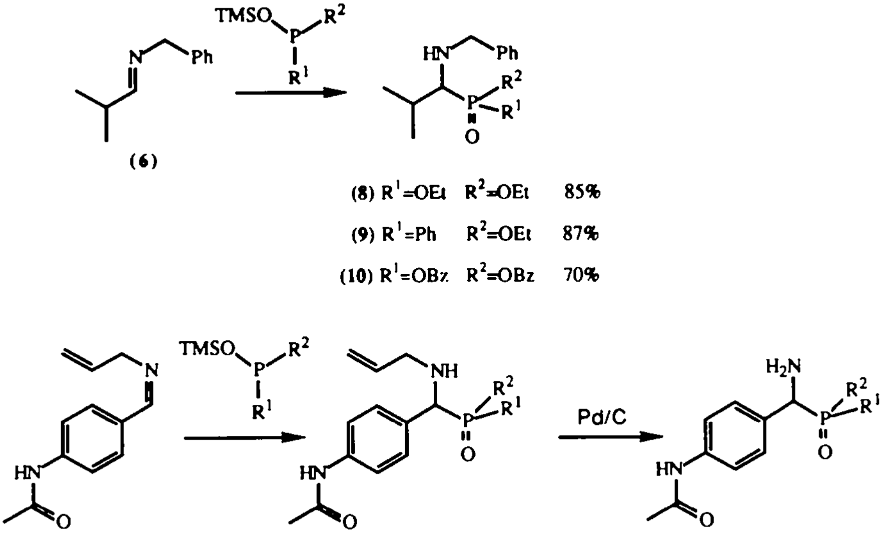


(1)

(2)

(5)

In order to establish the influence exerted by the substituents on phosphorus, an alkylimine (6) and an arylimine (7) were treated with a selection of phosphonites. The results (Scheme 2) show that the addition products were all formed in good to excellent (optimised) yields. The expected drop in yield with a change of substituent from EtO to Ph was not observed.



(6)

(8) R^1=OEt R^2=OEt 85%

(9) R^1=Ph R^2=OEt 87%

(10) R^1=OBz R^2=OBz 70%

(7)

(11) R^1=OEt R^2=OEt 95%

(12) R^1=Ph R^2=OEt 82%

(13) R^1=Ph R^2=OTMS(OH) 77%

(14) R^1=Ph R^2=Ph 95%

(15) R^1=OEt R^2=OEt 85%

(16) R^1=Ph R^2=OEt 66%

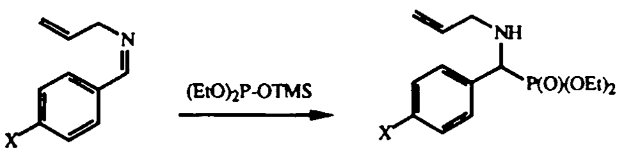
(17) R^1=Ph R^2=OH 95%

(18) R^1=Ph R^2=Ph 54%

Scheme 2

In the reaction of benzaldimines, where subsequent N-debenzylation would not be unambiguous, we employed the N-allyl group; this was readily removed from the addition product by treatment with palladium on charcoal in boiling ethanol.[9]

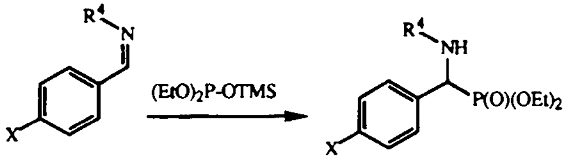
The influence of the imine substituent R^3 (Scheme 1) proved to be more interesting than expected. We prepared a series of N-allylimines from a variety of 4-substituted benzaldeydes and found, contrary to expectation, that on treatment with diethyl trimethylsilyl phosphite (3) under a standard set of conditions, electron-withdrawing substituents caused the reaction to be slower and the yields lower (see Scheme 3). The yields shown are those obtained after 15 hours at room temperature although in some cases reaction is virtually complete in a few hours. (The lower yields could be improved by increasing the reaction time or temperature).



X	NO_2	CN	Cl	H	NHAc	OMe
Imine	(19)	(20)	(21)	(22)	(7)	(23)
Product	(24)	(25)	(26)	(27)	(11)	(28)
Yield	55%	65%	69%	74%	85%	96%

Scheme 3

We also encountered an even more pronounced decelerating effect of electron withdrawing substituents when investigating other N-auxiliary groups, R^4 (Scheme 4). For example, N-4-nitrophenylimine (39) derived from 4-acetamidobenzaldehyde reacts *ca.* 400 times slower than the N-phenylimine (37) derivative of the same aldehyde, as shown by ^{31}P NMR monitoring of the initial reaction rates. The similarity between the substituent dependence rate profiles of this reaction and the acidic hydrolysis of imines[10] points to a similar mechanistic path (see below).

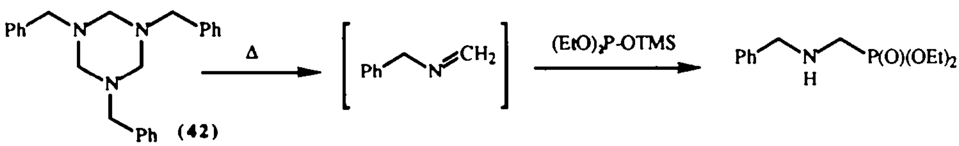


$X = O_2N$-	Imine	Product	Yield (%)
$R^4 = CH_2.CH{=}CH_2$	(19)	(24)	55
$R^4 = C(CH_3)_3$	(29)	(30)	53
R^4 = Ph	(31)	(32)	62
R^4 = NHPh	(33)	No Reaction	
R^4 = OBz	(34)	No Reaction	

X=AcNH-	Imine	Product	Yield (%)
$R^4 = CH_2.CH{=}CH_2$	(7)	(11)	85
$R^4 = C_6H_4.OMe$-*p*	(35)	(36)	92
R^4 = Ph	(37)	(38)	84
$R^4 = C_6H_4.NO_2$-*p*	(39)	(40)	74
R^4 = OBz	(41)	No Reaction	

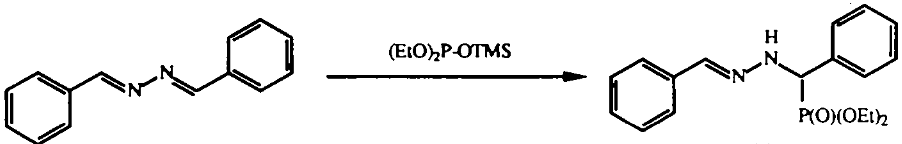
Scheme 4

1,3,5-Tribenzylhexahydro-1,3,5-triazine (42), a precursor of N-benzylmethanalimine, reacts with (3) only in boiling 1,2-dichloroethane, and then at the same rate as with diethyl phosphite itself, the rate determining step for the reaction being the fragmentation of the triazine.



(42)

In contrast with the N-aryl and N-alkyl imines which all underwent nucleophilic addition of the phosphorus (III) reagent (3), oxime ethers and hydrazones did not react at all. For example, benzaldehyde azine (43) gave only the mono adduct (44) which was inert to further reaction, and (45), (46), and (47) did not react.



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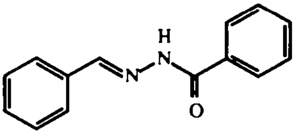

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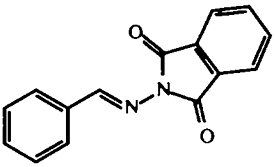

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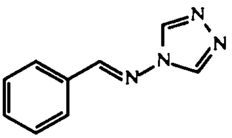
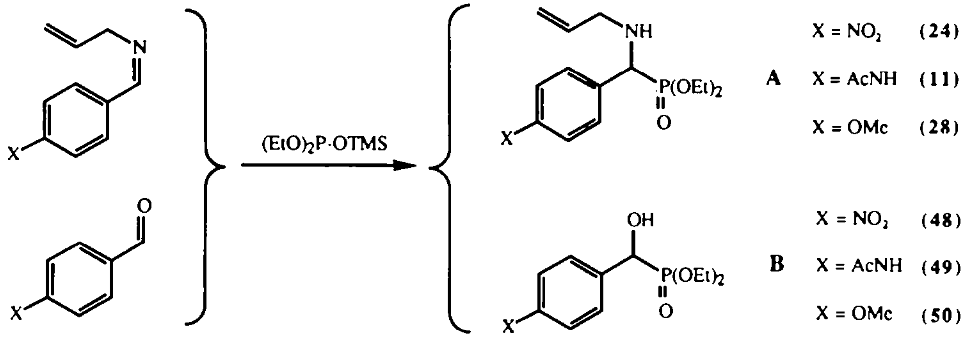


(47)

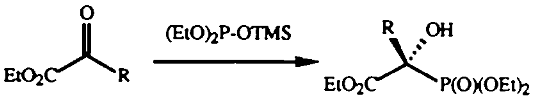
We also made a comparison of the reactivity of diethyl trimethylsilyl phosphite (3) towards other functionalities, particularly aldehydes and ketones, in order to be able to exploit the mild reaction conditions in functional group selectivity. We found that the addition of (3) to imines is considerably faster than addition to the parent aldehyde, and in competition experiments with equimolar amounts of reactant, addition occurred predominantly to the imine (Scheme 5).



X	NO_2	NHAc	OMe
A : B	100 : 0	93 : 7	72 : 28

Scheme 5

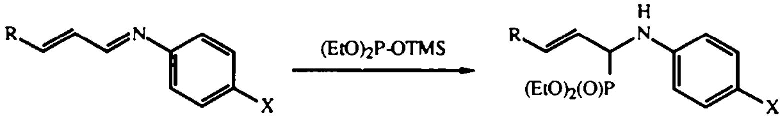
Addition of (3) to ketones is much slower than to aldehydes and only proceeds when there is strong electron withdrawal from the carbonyl group (Scheme 6). There was no reaction with 2-propanone, acetophenone, or benzophenone. Similarly there was no addition to aliphatic or aromatic nitriles, R-CN, where R= methyl, (4-nitrophenyl)methyl, ethoxycarbonyl, phenyl, 4-nitrophenyl and 4-methoxyphenyl.



R	Yield(Product)
(EtO)CO	76% (51)
Me	20% (52)

Scheme 6

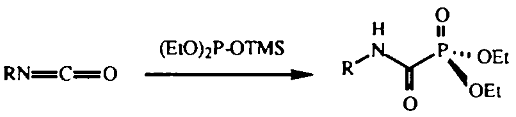
In order to establish the influence of electronic and steric effects on regioselectivity in the addition to α,β-unsaturated imines, we treated a range of N-aryl α,β-unsaturated imines with diethyl trimethylsilyl phosphite (3) and found that addition is exclusively 1,2- rather than 1,4-, regardless of the nature of the aryl substituent (Scheme 7).



R	X	Imine	Yield(Product)
Ph	NO_2	(53)	70% (54)
Ph	H	(55)	91% (56)
Ph	OMe	(57)	77% (58)
Me	H	(59)	55% (60)
Me	OMe	(61)	57% (62)

Scheme 7

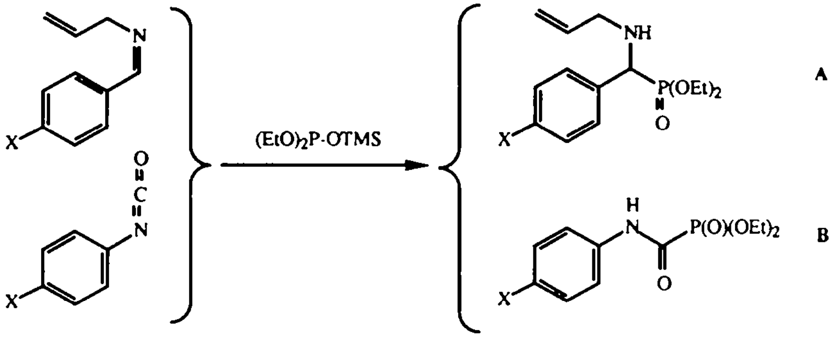
Of the other functional groups related to imines, isocyanates and carbodiimides are potentially



R	Yield(Product)
Phenyl	87% (63)
4-Nitrophenyl	86% (64)

Scheme 8

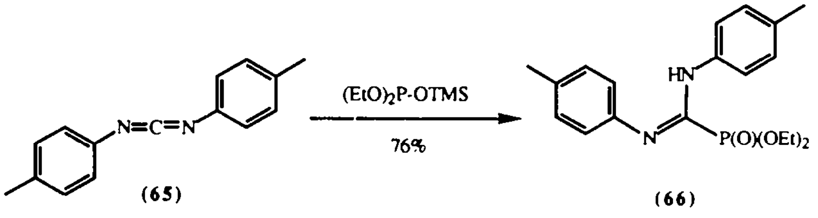
the most interesting as they could afford phosphonoureas[11] and phosphonoguanidines[12] respectively, analogues of two biologically important groups. Addition to aromatic isocyanates proceeded smoothly to give the adducts in good yields (Scheme 8). Competition experiments showed that the reactivity of the isocyanates, unlike that of imines, is enhanced by the presence of a powerfully electron withdrawing group (Scheme 9).



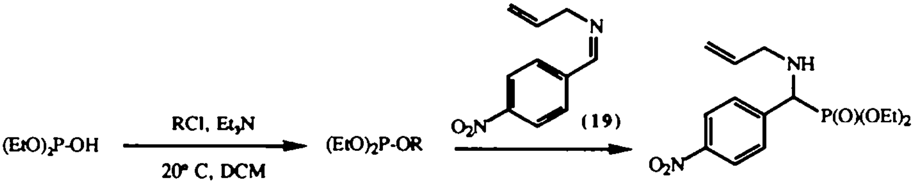
X	A:B
H	10:8
NO_2	1:10

Scheme 9

Addition to carbodiimides has, as yet, been observed only with the aromatic compound (**65**) which affords phosphonoguanidine (**66**). Surprisingly, there was no reaction with dicyclohexylcarbodiimide nor bis(trimethylsilyl)carbodiimide.



Finally, we report the results of a brief investigation into the influence of the silylating agent on the reaction between 4-nitrobenzaldehyde N-allylimine (**19**) and diethyl phosphite. We found, not surprisingly, that bulkier silyl groups, R, retarded both the formation of the silicon-phosphorus species and the addition reaction (Scheme 10). Indeed no silicon-phosphorus species was detected with chloro-t-butyldiphenylsilane as RCl and the adduct (**24**) from the 4-nitrophenyl imine presumably results from addition of the base-generated diethyl phosphite anion.



(24)

RCl	Reaction time (hours)	Yield (%)
Me$_3$SiCl	15	55
Me$_3$SiCl	60	85
Me$_3$SiCl	12*	65
^{t}BuMe$_2$SiCl	120	81
MePh$_2$SiCl	110	66
^{t}BuPh$_2$SiCl	112	24

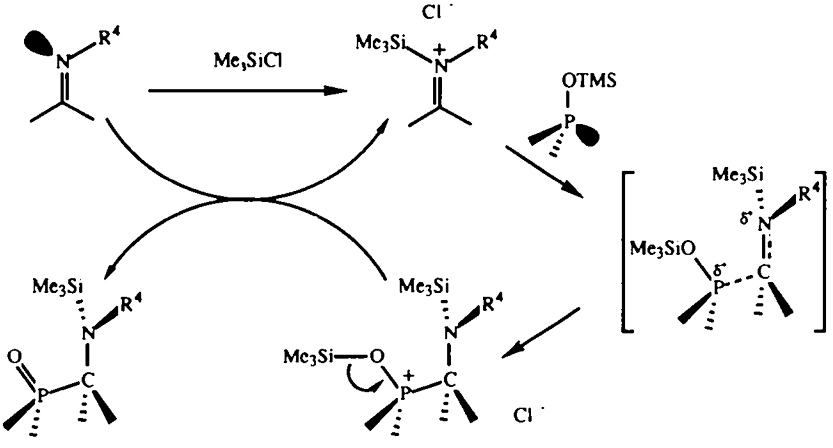
*at reflux

Scheme 10

Reaction Mechanism

From these results we can sketch a general mechanistic picture of the overall process. A more precise knowledge of the mechanistic details would be very useful in extending its synthetic scope and providing a better understanding of the addition of non-aggregated nucleophiles to *sp*^{2} carbon centers.

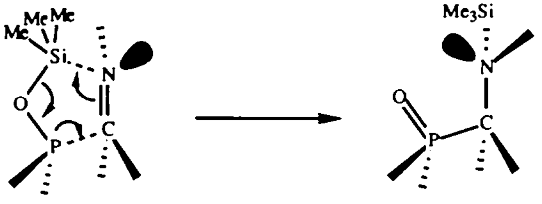
The spontaneous tautomerism of dialkyl phosphites and alkyl phenylphosphonites was shown[13] to lie overwhelmingly on the side of tetra-coordinated electrophilic species, R$_2$P(O)H, rather than the tri-coordinated nucleophilic species, R$_2$P(OH). Freezing out the latter by means of O-silylation[14] is thus expected to promote nucleophilic reactivity strongly.



(67)

Scheme 11

The observed electronic demand of the imine bond suggests that the rate determining step in this reaction incorporates nucleophilic attack by the imine nitrogen on an electrophilic species, presumably chlorotrimethylsilane, to form a transient iminium cation. Addition of the silyloxy P(III) species to this cation, accompanied by valency expansion at phosphorus, gives the N-silylated product and "TMS$^+$" either as regenerated chlorotrimethylsilane or by **(67)** itself acting as a silylating agent (Scheme 11). Hydrolytic work up cleaves the N-silyl group and affords the product. Alternatively a concerted 3+2 mechanism, as Evans has suggested for aldehydes,[5] could be operating (Scheme 12). If this is the case, then the transition state formation is presumably unsymmetrical with silicon-nitrogen bond formation more advanced than carbon-phosphorus bond formation.



Scheme 12

There has also been a great deal of effort invested in the chiral synthesis of α-aminophosphonic acids mainly by employment of chiral auxiliaries or resolution[1]. However diastereoselectivity in reactions where the phosphorus group itself is prochiral has not as yet been investigated, and we plan to report on this later.

Experimental

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. ^{1}H N.m.r spectra were obtained on a Jeol GSX300 spectrometer operating at 270 MHz and the solvents' residual proton signals were used as internal reference. ^{13}C N.m.r. spectra were obtained on a Jeol GSX300 operating at 68 MHz.^{31}P N.m.r spectra were obtained on a Jeol FXQ90 spectrometer operating at 36 MHz. A 0.1M solution of diethyl phosphite in $CDCl_3$ was used as an external reference (δ_P 6.50 p.p.m.) All chemical shifts are reported in p.p.m. with positive values being downfield from the standard. Coupling constants are reported in Hz. Infra-red spectra were measured on a Perkin-Elmer 1710 FTIR spectrometer. Mass spectra were obtained on an AE1 MS12 or a VG micromass 7070B mass spectrometer using electron impact (EI), chemical ionisation (CI) or fast atom bombardment (FAB) techniques.

Materials. Commercially available compounds were purified where necessary. Dichloromethane (DCM) was distilled from P_2O_5 and triethylamine was distilled from KOH under an inert atmosphere prior to use. Chlorotrimethylsilane was distilled and stored under argon. Ethyl acetate and petroleum ether b.p. 40-60°C (light petroleum) for chromatography and recrystallisations were distilled before use.

Imines. Unless otherwise stated, these were obtained by condensation of the relevant aldehyde and amine in dichloromethane or benzene solution from which water was removed by a Dean-Stark apparatus. They were purified by bulb-to-bulb distillation, crystallisation or chromatography as appropriate. Physical data are as follows:

2,2-Diethoxyethanal N-benzylimine (**1**). 2,2-Diethoxyethanal[15] (5.02g, 38mmol) was dissolved in dry dichloromethane (50 ml) and benzylamine (4.50 g, 40mmol) was added dropwise over 5 min with cooling. The mixture was left for 15 min and potassium carbonate (5 g) was added. After standing for 15 h at 4°C under a dry atmosphere of argon, the solid was filtered off and the solvent was evaporated to leave a yellowish oil which on distillation (b.p. 125° C at 1.2 mmHg) afforded *the title compound* as a colourless liquid (8.05 g, 96%), R_f 0.6 (silica gel, ether); (Found: MH^+ 222.1494. $C_{13}H_{20}NO_2$ requires 222.1494); ν_{max} (film) 3064, 3030, 2977, 2878, 1678 (C=N), 1497, 1454, 1374, 1291, 1123, 1062, 1028, 736 and 699 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.23 (6H, t, *J* 7Hz, 2 x CH_3), 3.64 (4H, m, 2 x CH_2 acetal), 4.62 (2H, s, $PhCH_2$), 4.83 (1H, d, *J* 5Hz, CH), 7.28 (5H, m, aromatic H) and 7.62 (1H, d, *J* 5Hz, CH=N); *m/z* (70 eV, 170° C) 177 (14), 103 (100), 91 (65) and 75 (46); *m/z* (CI, NH_3) 222 (MH^+, 100), 196 (65) and 103 (59).

2-Methylpropanaldehyde N-benzylimine (**6**),[16] b.p. 105°C/4 mmHg, $\nu_{max.}$ (C=N) 1671 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.39 [6 H, d, *J* 6 Hz, $(CH_3)_2C$], 2.75 (1 H, m, CH), 4.80 (2 H, d, *J* 1Hz, CH_2), 7.45-7.60 (5 H, m, aromatic H) and 7.90 (1 H, dt, *J* 5 Hz, 1 Hz, CH=N).

4-Acetamidobenzaldehyde N-allylimine (**7**), m.p. 141-142°C, (DCM / diethylether) (Found: C, 71.1; H, 6.9; N, 13.7. $C_{12}H_{14}N_2O$ requires C, 71.3; H, 7.0; N, 13.85%); $\nu_{max.}$ (nujol) 3288, 3252, 2955, 1665 (C=N), 1606 (C=O), 1551, 1512, 1408, 1326, 915, 839 and 529 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 2.18 (3H, s, CH_3CO), 4.24 (2H, m, allylic H), 5.15 (1H, dm, *Jcis* 10 Hz, $C=CH_{cis}$), 5.23 (1H, dm, *Jtrans* 17 Hz, $C=CH_{trans}$), 6.05 (1H, ddm, *Jtrans* 17 Hz, *Jcis* 10 Hz, -CH=), 7.57 (2H, d, *J* 8.5 Hz, aromatic H),7.68 (1H, s, NH), 7.70 (2H, d, *J* 8.5 Hz, aromatic H), 8.24 (1H, bs, CH=N); *m/z* (70 eV, 140°C) 202 (M^+, 100), 201 (84), 159 (64), 107 (82), 106 (79), 84 (64), 49 (85), 43 (84) and 41 (66).

4-Nitrobenzaldehyde N-allylimine (**19**),[17] m.p. 55-56°C, (DCM / light petroleum) (Found: C, 63.15; H, 5.2; N, 14.8. Calc. for $C_{10}H_{10}N_2O_2$: C, 62.85; H, 5.3; N, 14.7%); $\nu_{max.}$ (Nujol) 1647 (C=N), 1598, 1515, 1344, 1290, 1104, 1027, 983, 933, 858, 832 and 749 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 4.33 (2H, m, allylic H), 5.21(1H, dm, *Jcis* 10 Hz, $C=CH_{cis}$), 5.26 (1H, dm, *Jtrans* 17 Hz, $C=CH_{trans}$), 6.08 (1H, ddm, *Jtrans* 17 Hz, *Jcis* 10 Hz, -CH=), 7.92 (2H, d, *J* 8 Hz, aromatic H), 8.28 (2H, d, *J* 8 Hz, aromatic H), 8.39 (1H, bs, CH=N); *m/z* (70 eV, 130°C) 190 (M^+, 39), 189 (47), 173 (45), 143 (29), 116 (37), 89 (35), 41 (100) and 39 (32).

4-Cyanobenzaldehyde N-allylimine (**20**),[17] m.p. 25°C; b.p. 125°C/1 mmHg (Found: C, 77.5; H, 6.0; N, 16.5. Calc. for $C_{11}H_{10}N_2$: C, 77.6; H, 5.9; N, 16.5%); $\nu_{max.}$ (film) 2879, 2228 (C≡N), 1650 (C=N), 1413, 1372, 1303, 1287, 1021, 994, 921, 833 and 554 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 4.29 (2H, dm, allylic

H), 5.17 (1H, dm, *Jcis* 10 Hz, $C{=}CH_{cis}$), 5.23 (1H, dm, *Jtrans* 17 Hz, $C{=}CH_{trans}$), 6.05 (1H, ddm, *Jtrans* 17Hz, *Jcis* 10Hz, -CH=), 7.69 (2H, d, *J* 8 Hz, aromatic H), 7.84 (2H, d, *J* 8 Hz, aromatic H), 8.31 (1H, bs, CH=N); *m/z* (70 eV, 100°C) 170 (M^+, 80), 169 (100), 142 (75), 129 (30), 116 (30), 115 (40), 41 (70) and 39 (33).

4-Chlorobenzaldehyde N-allylimine (**21**), b.p. 100°C/0.05 mmHg (Found: C, 67.2; H, 5.5; N, 7.7. $C_{10}H_{10}NCl$ requires C, 66.9; H, 5.6; N, 7.8%); $\nu_{max.}$ (film) 2845, 1650 (C=N), 1596, 1573, 1490, 1407, 1297, 1088, 1015, 994, 920, 850, 822 and 505 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 4.25 (2H, m, allylic H), 5.16 (1H, dm, *Jcis* 10 Hz, $C{=}CH_{cis}$), 5.23 (1H, dm, *Jtrans* 17Hz, $C{=}CH_{trans}$), 6.06 (1H, ddm, *Jtrans* 17 Hz, *Jcis* 10 Hz, -CH=), 7.38 (2H, d, *J* 8 Hz, aromatic H), 7.69 (2H, d, *J* 8 Hz, aromatic H), 8.25 (1H, bs, CH=N); *m/z* (70 eV, 120°C) 180 (39), 179 (M^+, 66), 178 (100), 151 (45), 138 (34), 125 (33), 89 (36) and 41 (75)

Benzaldehyde N-allylimine (**22**),[17] b.p. 60°C/1mmHg (Found: C, 82.8; H, 7.8; N, 9.8. Calc. for $C_{10}H_{11}N$: C, 82.7; H, 7.6; N, 9.65%); $\nu_{max.}$ (film) 3063, 2843, 1650 (C=N), 1451, 1418, 1376, 1309, 1293, 1025, 993, 920, 755 and 694 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 4.27 (2H, m, allylic H), 5.16 (1H, dm, *Jcis* 10 Hz, $C{=}CH_{cis}$), 5.24 (1H, dm, *Jtrans* 17 Hz, $C{=}CH_{trans}$), 6.08 (1H, ddm, *Jtrans* 17 Hz, *Jcis* 10 Hz, -CH=), 7.40-7.43 (3H, m, aromatic H), 7.74-7.77 (2H, m, aromatic H), 8.30 (1H, bs, CH=N); *m/z* (70 eV, 70°C) 145 (M^+, 69), 144 (100), 117 (39), 104 (34), 91 (31), 90 (30), 41 (45) and 39 (23).

4-Methoxybenzaldehyde N-allylimine (**23**),[17] b.p. 100°C/0.07 mmHg (Found: C, 75.4; H, 7.6; N, 7.9. Calc. for $C_{11}H_{13}NO$: C, 75.4; H, 7.5; N, 8.0%); $\nu_{max.}$ (film) 2837, 1650 (C=N), 1607, 1579, 1512, 1306, 1252, 1167, 1033, 919, 832, and 529 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 3.84 (3H, s, CH_3O), 4.22 (2H, m, allylic H), 5.14 (1H, dm, *Jcis* 10 Hz, $C{=}CH_{cis}$), 5.22 (1H, dm, *Jtrans* 17 Hz, $C{=}CH_{trans}$), 6.06 (1H, ddm, *Jtrans* 17 Hz, *Jcis* 10 Hz, -CH=), 6.92 (2H, d, *J* 9 Hz, aromatic H), 7.70 (2H, d, *J* 9 Hz, aromatic H), 8.22 (1H, bs, CH=N); *m/z* (70 eV, 100°C) 175 (M^+, 75), 174 (100), 147 (17), 134 (29), 133 (19), 121 (30), 77 (18), 41 (44) and 39 (18).

4-Nitrobenzaldehyde N-^{t}butylimine (**29**), m.p. 74°C (Found: C, 63.9; H, 6.9; N, 13.5. $C_{11}H_{14}N_2O_2$ requires C, 64.0; H, 6.8; N, 13.6%); $\nu_{max.}$ (nujol) 1640, 1598, 1526, 1347, 1230, 1201, 1105, 1010, 958, 855, 835 and 751 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.315 (9 H, s, $(CH_3)_3C$), 7.91 (2 H, d, J 8.8 Hz, aromatic H), 8.26 (2 H, d, J 8.8 Hz, aromatic H) and 8.33 (1 H, s, CH=N); *m/z* (70 eV, 140°C) 206 (M^+, 5), 192 (7), 191 (60), 145 (14), 58 (5), 57 (100), 56 (4), 41 (16) and 39 (4).

4-Nitrobenzaldehyde N-phenylimine (**31**), m.p. 90-91°C (Lit.[18] 93°C) (Found: C, 69.2; H, 4.3; N, 12.5. Calc. for $C_{13}H_{10}N_2O_2$: C, 69.0; H, 4.5; N, 12.4%); $\nu_{max.}$ (nujol) 1599, 1516, 1465, 1356, 1316, 1096, 1072, 976, 853, 771, 746, 701 and 687 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.24 (3 H, m, aromatic H), 7.40-7.47 (2 H, m, aromatic H), 8.08 (2 H, d, *J* 9 Hz, 4-NO_2 aromatic H), 8.33 (2 H, d, *J* 9 Hz, 4-NO_2 aromatic H) and 8.56 (1 H, s, CH=N) ; *m/z* (70 eV, 100°C) 227 (15), 226 (M^+, 100), 225 (29), 180 (6), 179 (33), 104 (15), 77 (36), 51 (11) and 49 (31).

4-Acetamidobenzaldehyde N-(4-methoxyphenyl)imine **(35)**, m.p.184°C (DCM/ light petroleum) (Found: C, 71.4; H, 5.9; N, 10.4. $C_{16}H_{16}N_2O_2$ requires: C, 71.6; H, 6.0; N, 10.4%); $\nu_{max.}$ (nujol) 3279, 1665, 1624, 1607, 1587, 1542, 1510, 1413, 1316, 1251, 1031 and 839 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 2.21 (3 H, s, CH_3.CO), 3.83 (3H, s, OCH_3), 6.93 (2H, d, *J* 9 Hz, aromatic H), 7.22 (2H, d, *J* 9 Hz, aromatic H), 7.39 (1H, bs, NHAc), 7.62 (2H, d, *J* 8.5 Hz, aromatic H), 7.85 (2H, d, *J* 8.5 Hz, aromatic H) and 8.42 (1H, bs, CH=N); *m/z* (70 eV, 160°C) 269 (19), 268 (*M*$^+$, 100), 253 (21), 226 (16), 212 (10), 211 (51), 107 (11), 92 (12) and 43 (18).

4-Acetamidobenzaldehyde N-phenylimine **(37)**, m.p. 137-141°C (DCM/ diethylether) (Found: C, 75.5; H, 5.9; N, 11.6. $C_{15}H_{14}N_2O$ requires C, 75.6; H, 5.9; N, 11.7%); $\nu_{max.}$ (nujol) 3245, 1662, 1624, 1593, 1533, 1410, 1321, 1264, 1170, 841, 761, 721, 698 and 545 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 2.12 (3 H, s, CH_3CO), 7.18-7.25 (2 H, m, aromatic H), 7.36-7.44 (3 H, m, aromatic H and NHAc), 7.64 (2 H, d, *J* 9 Hz, aromatic H), 7.87 (2 H, d, *J* 9 Hz, aromatic H) and 8.40 (1 H, s, CH=N); *m/z* (70 eV, 140°C) 239 (17) , 238 (*M*$^+$, 100), 197 (11), 196 (76), 195 (75), 107 (11), 77 (30), 51 (11) and 43 (19).

4-Acetamidobenzaldehyde N-(4-nitrophenyl)imine **(39)**, m.p. 231-232°C (DCM/ light petroleum) (Found *M*$^+$ 283.0957. $C_{15}H_{13}N_3O_3$ requires 283.0957); ν_{max} (nujol) 3309, 3187, 1676, 1598, 1582, 1530, 1510, 1412, 1342, 1324, 1268 and 1168 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 2.23 (3 H, s, CH_3CO), 7.24 (2 H, d, *J* 9Hz, aromatic H), 7.40 (1H, bs, NHAc), 7.68 (2 H, d, *J* 9Hz, aromatic H), 7.89 (2 H, d, *J* 9Hz, aromatic H) and 8.26 (2 H, d, *J* 9Hz, aromatic H) and 8.36 (1 H, s, CH=N) ; *m/z* (70 eV, 180°C) 283 (*M*$^+$, 10), 241 (11), 163 (50), 121 (71), 120 (100), 92 (18), 65 (21) and 43 (54).

Oximes **(34)** *and* **(41)** were prepared by dehydrative condensation of the aldehyde and O-benzylhydroxy ammonium chloride in benzene in the presence of poly(4-vinylpyridine). Physical data are as follows:

4-Nitrobenzaldehyde O-benzyloxime **(34)**,[19] m.p. 118-119°C, (DCM/ light petroleum) (Found: C, 65.5; H, 4.6; N, 10.9. Calc. for $C_{14}H_{12}N_2O_3$: C, 65.6; H, 4.7; N, 10.9%); $\nu_{max.}$ (nujol) 3030, 1588, 1456, 1343, 1105, 1080, 1027, 937, 853, 837, 750 and 688 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 5.265 (2H, s, CH_2), 7.34-7.44 (5 H, m, aromatic H), 7.74 (2 H, d, J 9.5 Hz, 4-NO_2 aromatic H), 8.18 (1 H, s, CH=N) and 8.22 (2 H, d, J 9.5 Hz, 4-NO_2 aromatic H); *m/z* (70 eV, 140°C) 256 (1, *M*$^+$), 92 (9), 91 (100), 77 (4), 76 (2), 65 (5), 63 (2), 51 (3) and 50 (2).

4-Acetamidobenzaldehyde O-benzyloxmine **(41)**, m.p. 105-115°C (Found: C, 71.5; H, 5.9; N, 10.35. $C_{16}H_{16}N_2O_2$ requires C, 71.6; H, 6.0; N, 10.4%); ν_{max} (nujol) 3244, 1665, 1596, 1538, 1515, 1455, 1408, 1370, 1322, 1271, 1038, 932 and 745 cm^{-1}; δH (270 MHz, $CDCl_3$) 2.18 (3H, s, CH_3CO), 5.20 (2H, s, CH_2), 7.31-7.44 (5 H, m, aromatic H and NHAc), 7.53 (4 H, m, aromatic H), and 8.09 (1 H, s, CH=N); *m/z* (70 eV, 200°C) 268 (21, *M*$^+$), 119 (7), 118 (14), 91 (100), 77 (8), 65 (8) and 43 (16).

Benzaldimines **(45)**, m.p. 204°C (Lit.[20] 206°C), **(46)**, m.p. 163°C (Lit.[21] m.p. 166°C) and **(47)** m.p. 170°C (Lit.[22] m.p. 169-170°C) were prepared from benzaldehyde and the relevent amine in refluxing ethanol and were recrystallized from ethanol.

Cinnamaldehyde N-(4-methoxyphenyl)imine(**57**),[23a] m.p. 120°C, (DCM / light petroleum) (Found: C, 80.7; H, 6.3; N, 5.9. Calc. for $C_{16}H_{15}NO$: C, 81.0; H, 6.4; N, 5.9%); ν_{max} (Nujol) 1629, 1605, 1575, 1505, 1288, 1250, 1179, 1164, 1154, 1111, 1032, 988, 960, 838, 759, 747 and 695 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 3.83 (3H, s, OCH_3), 6.92 (2H, d, *J* 9 Hz, p-MeO aromatic H), 7.21 (2H, d, *J* 9 Hz, p-MeO aromatic H), 7.34-7.43 (3H, m, aromatic H), 7.11 (1H, d, *J* 4 Hz), 7.12 (1H, d, *J* 5Hz), 7.52-7.55 (2H, m, aromatic H), 8.30 (1H, dd, *J* 4 Hz, 5 Hz, CH=N); *m/z* (70 eV, 120°C) 238 (10), 237 (M^+, 59), 236 (100), 122 (4), 115 (23),92 (4), 77 (6) and 64 (4).

Cinnamaldehyde N-phenylimine(**55**),[23a] m.p. 107°C, (DCM / light petroleum) (Found: C, 86.7; H, 6.1; N, 6.6. Calc. for $C_{15}H_{13}N$: C, 86.9; H, 6.3; N, 6.8%); $\nu_{max.}$ (Nujol) 1623, 1599, 1573 (C=N), 1303, 1148, 1074, 995, 959, 914, 770, 750, 688 and 635 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.10-7.21 (5H, m, aromatic and vinylic H), 7.32-7.40 (5H,m, aromatic H), 7.48 (2H, m, aromatic H), 8.24 (1H, dd, *J* 6 Hz, 2 Hz, CH=N); *m/z* (70 eV, 100°C) 207 (42), 206 (M^+, 100), 115 (6) and 77 (18).

Cinnamaldehyde N-(4-nitrophenyl)imine (**53**),[23b] m.p. 115°C, (DCM / light petroleum) (Found: C, 71.6; H, 4.9; N, 11.2. Calc. for $C_{15}H_{12}N_2O_2$: C, 71.4; H, 4.8; N, 11.1%); ν_{max} (Nujol) 1630, 1597, 1578, 1513, 1337, 1207, 1159, 1105, 989, 964, 872, 856, 844, 753, 696, 667, 633, 530 and 513 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 6.85 (1H, dd, *J* 9 Hz, 12 Hz, αH), 7.22 (2H, d, *J* 9 Hz, p-NO_2 aromatic H), 7.27 (1H,d, *J* 12 Hz, βH), 7.40-7.45 (3H, m, aromatic H), 7.55-7.59 (2H, m, aromatic H), 8.23 (1H, d, *J* 9 Hz, CH=N), 8.26 (2H, d, *J* 9 Hz, p-NO_2 aromatic H); *m/z* (70 eV, 150°C) 252 (M^+, 44), 251 (100), 206 (8), 205 (45), 204 (12), 115 916), 103 (7) and 76 (9).

Crotonaldehyde N-phenylimine and *crotonaldehyde N-(4-methoxyphenyl)imine* were unstable and were therefore distilled directly into the reaction vessel for the next step.

Typical experimental procedure for the condensation of diethyl phosphite with imines. Chlorotrimethylsilane (0.35 ml, 1.1 eq) was delivered to a stirring solution of diethyl phosphite (0.35 g, 2.53 mmol) and triethylamine (0.39 ml, 1.1 eq) in dichloromethane (50 ml) maintained at 0° C and under an atmosphere of argon.[Formation of the tricoordinated phosphorus species may be checked by n.m.r. monitoring of the reaction. The following are the ^{31}P signals in deuterodichloromethane (δD_3PO_4=O): diethyl trimethylsilyl phosphite, 128.4 (Lit[14]: 128) ppm; ethyl trimethylsilyl phenylphosphonite, 147.0 ppm; bis(trimethylsiyl) phenylphosphonite, 141.9 ppm; trimethylsilyl diphenylphosphinite, 95.3 (Lit[14]: 94.1) ppm.]. The imine (2.53 mmol) was added after 15 min and the solution was brought to room temperature. If refluxing was required it was carried out under argon. The reaction mixture was poured into water (50 ml) and organic products were extracted with dichloromethane (2 X 75 ml). Combined organic extracts were dried ($NaSO_4$) and evaporated. The residue was chromatographed (silica gel 60H) to afford the required compounds, the data for which are as follows:

Diethyl 1-(benzylamino)-2,2-(diethoxy)ethanephosphonate (**2**), yield 76%, oil (Found: C, 57.0; H, 8.5; N, 4.1. $C_{17}H_{29}NO_5P$ requires C, 57.0; H, 8.2; N, 3.9%); ν_{max} (film) 2979, 2905, 1455, 1392, 1373, 1343, 1245, 1109, 1029, 966, 734, 700 and 666 cm^{-1}; δ_H (90MHz, $CDCl_3$) 1.2 (6H, t, *J* 7Hz, acetal CH_3), 1.33 (6H, dt, *J* 5Hz, 7Hz), 3.1 (1H, dd, *J* 15Hz, 4Hz, CH), 3.4-3.75 (4H, m, CH_2's), 4.0-4.2 (6H, m, CH_2's) , 4.76 (1H, t, *J* 4Hz, acetal CH), 7.2-7.4 (5H,m); *m/z* (70 eV, 100°C) 359 (M^+, 3), 313 (14), 256 (10), 110 (25), 103 (89), 91 (100) and 83 (24).

Butyl [1-(benzylamino)-2,2-(diethoxy)ethane]phenylphosphinate (**5**) , yield 81%, oil, (Found M^+ 419.2225. $C_{23}H_{34}NO_4P$ requires 419.2225); $\nu_{max.}$ (film) 2973, 2932, 2874, 1455, 1440, 1373, 1341, 1226 , 1120(s) 1063 (s), 1024 (s), 975, 734 and 698 cm^{-1}; δ_H(270 MHz, $CDCl_3$) 0.95(3H, t, *J* 7Hz), 1.05 (3H, t, *J* 7Hz), 1.2 (3H, t, *J* 7Hz), 1.3-1.5 (2H, sextet, *J* 7Hz), 1.6-1.75 (2H, quintet, J 7Hz), 2.15 (bs, 1H), 3.2 (1H, dd, *J* 5Hz, 14Hz), 3.25-4.15 (8H, m), 4.8 (1H, t, *J* 5Hz), 7.2-7.25 (5H, m), 7.4-7.6 (3H, m), 7.75-7.9 (2H, m), *m/z* (70 eV, 100° C) 419 (M^+, 0.6), 373 (64), 344 (31), 143 (46), 91 (100), 84 (45).

Diethyl 2-methyl-1-(benzylamino)propanephosphonate (**8**), yield 85%, b.p. 180°C/0.5 mbar, (Found: C, 60.2; H, 8.9; N, 4.7. $C_{15}H_{26}NO_3P$ requires C, 60.2; H, 8.75; N, 4.7%); $\nu_{max.}$ (film) 3475, 2978, 2932, 2906, 1455, 1391, 1245, 1164, 1055, 1029, 960, 795, 741, and 701 cm^{-1}; δ_H(270 MHz, $CDCl_3$) 1.00 [3H, d, *J* 7Hz, $(CH_3)_2C$], 1.01 (3H, dd, *J* 7Hz, 1 Hz, ^{i}Pr CH_3), 1.33 (6H, dt, *J* 7Hz, 1 Hz, 2 X CH_3 of EtO), 1.8 (1H, bs, NH), 2.14 (1H, m, Me_2CH), 2.73 (1H, dd, *J* 15Hz, 4Hz, α-H), 3.83 (1H, dd, *J* 13Hz, 2Hz, benzylic H), 4.03 (1H, dd, *J* 13 Hz, 1 Hz), 4.06-4.21 (4H, m, CH_2's), 7.2-7.66 (5H, m, aromatic H), $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 27.9 ppm, *m/z* (70 eV, 140°C) 299 (M^+, 1), 162 (45), 161 (17), 111 (18), 92 (17), 91 (100), 83 (17), 65 (13), and 45 (5).

Ethyl [2-methyl-1-(benzylamino)propane]phenylphosphinate (**9**), yield 87% of a 2:1 diastereomeric mixture the minor diasteromer of which was obtained crystalline: m.p. 103-105°C (Found: C, 68.6; H, 8.0; N, 4.2. $C_{19}H_{26}NO_2P$ requires C, 68.9; H, 7.9; N, 4.2%); $\nu_{max.}$ (nujol) 3283, 1437, 1220, 1117, 1032, 941, 767, 746, 732, 699, 564 and 516 cm^{-1}; δ_H (270MHz, $CDCl_3$) 0.93 (3H, dd, *J* 7Hz, 1Hz, CH_3), 0.95 (3H, d, *J* 7Hz, CH_3), 1.33 (3H, t, *J* 7Hz, CH_3 of EtO), 1.88 (1H, bm, NH), 2.86 (2H, dd, *J* 10Hz, 3Hz, CH_2Ph), 3.77-3.99 (2H, m, CH_2Me), 4.14 (1H, dhept, *J* 10Hz, 7Hz, CH), 7.21-7.31 (5H, m, benzylic aromatic H), 7.43-7.58 (3H, m, aromatic H) and 7.78-7.85 (2H, m, aromatic H); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 43.5 ppm; *m/z* (70 eV, 210°C) 331 (M^+, 0.1), 162 (43), 142 (11), 141 (11), 92 (16), 91 (100), 79 (12), 78 (16) and 77 (14).

Dibenzyl 2-methyl-1-(benzylamino)propanephosphonate (**10**), yield 70%, oil, (Found: C, 70.7; H, 7.3; N, 3.3. $C_{25}H_{30}NO_3P$ requires C, 70.9; H, 7.1; N, 3.0%); ν_{max} (film) 3064, 3032, 2960, 2890, 1497, 1456, 1381, 1245, 1081, 996, 919, 866, 798, 736, 698, 599, 548 and 494 cm^{-1}; δ_H (270MHz, $CDCl_3$) 0.98 (3H, d, *J* 7Hz, 2Hz, CH_3), 1.00 (3H, dd, *J* 7Hz, 2Hz, CH_3), 1.75 (1H, bs, NH), 2.17 (1H, dhept, *J* 16Hz, 7Hz, H-2), 2.80 (2H, dd, *J* 14Hz, 4Hz, H-1), 3.79 (1H, dd, *J* 23Hz, 2Hz, benzylic H), 3.98 (1H, dd, *J* 13Hz, 2Hz, benzylic H), 4.92-5.14 (4H, m, CH_2Me), 7.2-7.39 (5H, m, aromatic H); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 28.8 ppm; *m/z* (70 eV, 170°C) 423 (M^+, 0.1), 180 (9), 171 (36), 163 (25), 162 (10), 107 (13), 92 (14), 91 (100) and 65 (11).

Diethyl (4-acetamidophenyl)allylaminomethanephosphonate (**11**), yield 95%, m.p. 141-142°C (DCM/diethyl ether) (Found: C, 56.55; H, 7.5; N, 8.1. $C_{16}H_{25}N_2O_4P$ requires C, 56.5; H, 7.4; N, 8.2%); $\nu_{max.}$ (nujol) 3306, 3256, 3190, 3121, 3069, 1684, 1603, 1544, 1514, 1415, 1317, 1230, 1183, 1163, 1101, 1030, 960, 910, 875, 850, 795, 754, and 578 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.17 (3 H, t, J 7Hz, CH_3 of EtO), 1.31 (3 H, t, J 7Hz, CH_3 of EtO), 1.34 (1 H, bs, NH), 2.17 (3 H, s, CH_3CO), 3.00 (1H, dd, J 6Hz, J 14Hz, allylic H), 3.21 (1H, dd, J 6Hz, J 1Hz, allylic H), 3.80-4.17 (5 H, m, CH_2's and PhCH), 5.07 and 5.13 (2 H, m, $=CH_2$), 5.73-5.87 (1 H, m, -CH=), 7.28 (2 H, dd, J_{HH} 8Hz, J_{HP} 2Hz, aromatic H), 7.47 (2 H, d, J 8Hz, aromatic H)and 8.77 (1 H, bs, AcNH); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 22.75 ppm; *m/z* (70 eV, 160°C) 340 (M^+, 2), 203 (100), 202 (70), 201 (60), 111 (70), 83 (75), 65 (60), 43 (54), and 41 (53).

Ethyl [(4-acetamidophenyl)allylaminomethane]phenylphosphinate(**12**), yield 82% (of 2:1 diastereomeric mixture), m.p. 55-65°C (Found: C, 64.4; H, 6.8; N, 7.5. $C_{20}H_{25}N_2O_3P$ requires C, 64.5; H, 6.8; N, 7.5%); $\nu_{max.}$ (nujol) 3261, 1689, 1603, 1542, 1510, 1411, 1315, 1264, 1214, 1035, 957, 722, 694, 569, and 548; δ_H (270 MHz, $CDCl_3$) (* refers to the distinguishable signals of the minor diastereomer) 1.18* and 1.32 (3 H, t, J 7Hz, CH_3), 1.97 (1H, bs, NH), 2.13* and 2.16 (3 H, s, $COCH_3$), 2.91* and 2.98 (1 H, dd, J 7Hz, 15 Hz, allylic H), 3.17* and 3.23 (1 H, ddm, J 5Hz, 16 Hz, allylic H), 3.85-4.20 (3H, m, CH_2 and PhCH), 4.94-5.07 (2 H, m, $=CH_2$), 5.55-5.83 (1H, m, -CH=), 7.01-7.75 (9H, m, aromatic H), 8.83 and 9.07* (1H, bs, AcNH); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 38.8 (major) and 38.0 (minor) ppm; *m/z* (70 eV, 150°C) 372 (M^+, 1), 203 (65), 202 (67), 170 (62), 142 (79), 141 (64), 79 (70), 78 (100) and 77 (87).

[(4-Acetamidophenyl)allylaminomethane]phenylphosphinic acid (**13**), yield 77%, m.p. 217°C (water/ethanol) (Found: C, 61.3; H, 6.2; N, 8.0. $C_{18}H_{21}N_2O_3P.{}^1/_2H_2O$ requires C, 61.2; H, 6.3; N, 7.9%); $\nu_{max.}$ (nujol) 3301, 3256, 2726, 2618, 1667, 1600, 1538, 1417, 1330, 1199, 1130, 1044, 1025, 947, 861, 836, 757, 720, 698, and 554 cm^{-1}; δ_H (270 MHz, DMSO-d_6) 2.00 (3 H, s, CH_3), 3.19 (1H, dd, J 13Hz, J 9Hz, allylic H), 3.50 (1H, bd, J 14Hz, allylic H), 4.13 (1H, d, J 11Hz, CH), (1H, d, J 17Hz, $=CH_2$) and 5.13 (1 H, d, J 11Hz, $=CH_2$), 6.10 (1 H, m, -CH=), 7.16-7.50 (9 H, m, aromatic H) and 9.25 (1 H, bs, AcNH); $\delta_P\{H\}$ (36 MHz, D_2O) 30.8 ppm; *m/z* (FAB, Glycerol) 345 (MH^+, 9), 289 (4), 203 (100), 163 (14), 75 (24), 57 (22) and 45 (20).

[(4-Acetamidophenyl)allylaminomethyl]diphenylphosphine oxide (**14**), yield 95%, m.p. 211-214°C (Found: C, 71.4; H, 6.3; N, 6.95. $C_{24}H_{25}N_2O_2P$ requires C, 71.3; H, 6.2; N, 6.9%); $\nu_{max.}$ (nujol) 1680, 1603, 1542, 1510, 1415, 1317, 1267, 1175, 1117, 722, 698, 561, 530 and 514 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 2.13 (3 H, s, CH_3), 2.99 (1H, dd, J 13Hz, J 7Hz, allylic H), 3.26 (1H, dd, J 14Hz, J 5Hz, allylic H), 4.25 (1H, d, J 11Hz, CH), 5.00 and 5.06 and 5.10 (2 H, m, $=CH_2$), 5.75 (1 H, m, -CH=), 7.25 (2 H, dd, J_{HH} 9Hz, J_{HP} 2Hz, aromatic H), 7.30-7.64 and 7.81-7.89 (12 H, m, aromatic H), and 8.50 (1 H, bs, AcNH); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 30.6 ppm; *m/z* (70 eV, 210°C) 202 (54), 201 (100), 159 (19), 132 (15), 124 (22), 78 (21), 77 (27), 51 (18), and 43 (54); *m/z* (FAB, 3-Nitrobenzylalcohol) 405 (MH^+, 5), 203 (93), 107 (32), 90 (25), 89 (28) and 77 (35).

Removal of N-allyl groups. The N-allyl compound was dissolved in ethanol and palladium on charcoal (10%) was added. The mixture was refluxed until the reaction was complete, as detected by tlc analysis. The solid was filtered off and the ethanol was removed at reduced pressure. The residue was chromatographed on alumina directly to afford the required compounds, the physical data for which are as follows:

Diethyl (4-acetamidophenyl)aminomethanephosphonate (**15**), yield 85%, m.p. 105-108°C (chloroform/ ether), (Found: C, 52.05; H, 7.0; N, 9.15. $C_{13}H_{21}N_2O_4P$ requires C, 52.0; H, 7.05; N, 9.3%); ν_{max} (nujol) 3259, 3191, 3123, 1687 (C=O), 1605, 1543, 1515,1414, 1319, 1268, 1224, 1049, 1019, 962, 847, 787, 580 and 553 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.20 (3 H, t, *J* 7Hz, CH_3), 1.29 (3 H, t, *J* 7Hz, CH_3), 1.78 (2H, bs, NH_2), 2.16 (3 H, s, $COCH_3$), 3.80-4.09 (4 H, m, CH_2's), 4.23 (1H, d, *J* 16 Hz, CH), 7.33 (2H, d, J_{HH} 8 Hz, J_{HP} 2 Hz, aromatic H), 7.47 (2H, d, *J* 8 Hz, aromatic H) and 8.29 (1H, bs, NHAc); δ_P{H} (36 MHz, $CDCl_3$) 23.8 ppm; *m/z* (70 eV, 180°C) 300 (M^+, 1), 164 (10), 163 (100), 121 (22), 120 (14), 119 (11), 94 (7), 83 (8) and 43 (10).

Ethyl [(4-acetamidophenyl)aminomethane]phenylphosphinate (**16**), yield 66%,(Found: MH^+ 333.1368. $C_{17}H_{22}N_2O_3P$ requires 333.1368); ν_{max} (film) 3256, 3187, 3118, 3058, 2984, 1674, 1605, 1540, 1515, 1439, 1412, 1372, 1319, 1268, 1207, 1121, 1035, 958, 845, 721, 697 and 549 cm^{-1}; δ_H (270 MHz, $CDCl_3$) (* refers to the distinguishible signals of the minor diastereomer) 1.23* and 1.33 (3 H, t, *J* 7Hz, CH_3), 1.81 (2H, bs, NH_2), 2.12* and 2.15 (3 H, s, $COCH_3$), 3.85-4.20 (2H, m, CH_2), 3.39 and 4.36* (1H, d, *J* 11 Hz, *J* 13 Hz*, benzylic H), 7.01-7.75 (9H, m, aromatic H), 9.09 and 9.29* (1H, bs, AcNH) ; δ_P{H} (36 MHz, $CDCl_3$) 39.35 (major) and 39.15 (minor) ppm; *m/z* (FAB, NoBA) 333 (MH^+, 7).

[(4-Acetamidophenyl)aminomethane]phenylphosphinic acid (**17**), yield 95%, m.p. 212-213°C (water/ ethanol), (Found: C, 55.95; H, 6.1; N, 8.6. $C_{15}H_{17}N_2O_3P.H_2O$ requires C, 55.9; H, 5.9; N, 8.7%); $\nu_{max.}$ (nujol) 1667, 1599, 1520, 1418, 1323, 1271, 1173, 1130, 1044, 1021, 843, 748, 719, 692, 629, 550 and 509 cm^{-1}; δ_H (270 MHz, D_2O) 1.97 (3H, s, $COCH_3$), 4.32 (1H, d, J_{HP} 12Hz, CH), 7.00-7.43 (10H, m, aromatic H); δ_P (36 MHz, D_2O) 24.0 ppm; *m/z* (70 eV, 240°C) 148 (18), 121 (100), 120 (24), 119 (23), 106 (64), 94 (20), 78 (21), 77 (20) and 43 (39).

[(4-Acetamidophenyl)aminomethyl]diphenylphosphine oxide (**18**), yield 55%, m.p. 127-130°C (Found: 201.0469. $C_{10}H_{10}OP$ requires 201.0469); $\nu_{max.}$ (film) 3253, 3186, 3115, 3059, 1683, 1603, 1549, 1513, 1438, 1413, 1371, 1318, 1271, 1178, 1120, 1100, 1072, 999, 911, 846, 726, 696 and 647 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 2.09 (3 H, s, $COCH_3$), 6.75 (1H, d, *J* 10Hz), 7.22-7.77 (14H, m, aromatic H), 9.78 (1H, bs, AcNH); δ_P{H} (36 MHz, $CDCl_3$) 31.3 ppm; *m/z* (70 eV, 110°C) 201 ($Ph_2P=O^+$, 100), 77 (45) and 45 (13).

Diethyl allylamino(4-nitrophenyl)methanephosphonate (**24**), yield 50%, m.p. 50-51°C (Found: C, 51.1; H, 6.5; N, 8.5. $C_{14}H_{21}N_2O_5P$ requires C, 51.2; H, 6.45; N, 8.5%); $\nu_{max.}$ (nujol) 3299, 1520, 1466, 1366, 1348, 1234, 1188, 1109, 1051, 943, 924 and 755 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.20 (3H, t, *J* 7Hz, CH_3),1.27 (3H, t, *J* 7Hz, CH_3), 2.07 (1H, bs, NH), 2.99 (1H, dd, *J* 7Hz,14Hz, allylic H), 3.20 (1H, dd, J 7Hz, 14Hz, allylic H), 3.92-4.13 (4H, m, CH_2's), 4.21 (1H, d, J_{HP} 21 Hz, CH), 5.04-5.12 (2H, m, $=CH_2$), 5.71-5.86 (1H, m, -CH=), 7.59 (2H, dd, J_{HH} 8.5 Hz, J_{HP} 2.2 Hz, aromatic H) and 8.20 (2H, d, J_{HH} 8.5 Hz, aromatic H); δ_P{H} (36 MHz, $CDCl_3$) 21.0 ppm; *m/z* (70 eV, 140°C) 328 (M^+, 2), 192 (12), 191 (100), 190 (3), 179 (6), 145 (8), 117 (2), 56 (4), and 41 (30).

Diethyl allylamino(4-cyanophenyl)methanephosphonate (**25**), yield 65%, m.p. 39-40°C (Found: C, 58.7; H, 6.85; N, 9.1. $C_{15}H_{21}N_2O_3P$ requires C, 58.4; H, 6.9; N, 9.1%); $\nu_{max.}$ (film) 2983, 2229, 1608, 1392, 1247, 1164, 1099, 1025, 970, 872, 788, 754, 578, and 489 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.18 (3H, t, J 7Hz, CH_3), 1.26 (3H, t, J 7Hz, CH_3), 2.03 (1H, bs, NH), 2.97 (1H, dd, J 7Hz, 14Hz, allylic H), 3.20 (1H, dd, J 6Hz, 16Hz, allylic H), 3.88-4.11 (4H, m, CH_2's), 4.14 (1H, d, J_{HP} 21 Hz, CH), 5.06 (1H, dm, J 9.5 Hz, $=CH_2$), 5.11 (1H, bs, $=CH_2$), 5.70-5.85 (1H, m, -CH=), 7.52 (2H, dd, J_{HH} 8 Hz, J_{HP} 2 Hz, aromatic H) and 7.625 (2H, d, J_{HH} 8 Hz, aromatic H) ; δ_P{H} (36 MHz, $CDCl_3$) 21.2 ppm; *m/z* (70 eV, 100°C) 308 (M^+, 3), 172 (13), 171 (100), 111 (18), 99 (10), 83 (17), 65 (14), 41 (37), and 29 (10).

Diethyl allylamino(4-chlorophenyl)methanephosphonate (**26**), yield 69%, m.p. 15°C (Found: C, 52.9; H, 6.7; N, 4.4. $C_{14}H_{21}NO_3PCl$ requires C, 52.75; H, 6.7; N, 4.3%); ν_{max} (film) 2982, 2908, 1490, 1445, 1408, 1392, 1244, 1164, 1093, 1025, 966, 868, 836, 787, 754 and 569 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.17 (3H, dt, J_{HH} 7Hz, J_{HP}0.5 Hz, CH_3),1.27 (3H, dt, J_{HH} 7Hz, J_{HP}0.5 Hz, CH_3), 1.95 (1H, bs, NH), 2.98 (1H, ddm, J 7Hz, 14Hz, allylic H), 3.21 (1H, ddm, J 5Hz, 14Hz, allylic H), 3.845-4.12 (4H, m, CH_2's), 4.055 (1H, d, J_{HP} 21 Hz, CH), 5.045-5.12 (2H, m, $=CH_2$), 5.72-5.86 (1H, m, -CH=), 7.33 (4H, m, aromatic H); δ_P{H} (36 MHz, $CDCl_3$) 22.2 ppm; *m/z* (70 eV, 120°C) 319 (2), 317 (M^+, 5), 182 (33), 181 (13), 180 (100), 179 (7), 178 (6),125 (5), 41 (17) and 32 (11).

Diethyl allylamino(phenyl)methanephosphonate (**27**), yield 74%, oil (Found: M^+ 283.1342. $C_{14}H_{22}NO_3P$ requires 283.1337); $\nu_{max.}$ (film) 2981, 2908, 1494, 1455, 1392, 1244, 1164, 1099, 1028, 967, 789, 701 and 568 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.14 (3 H, t, J 7Hz, CH_3), 1.285 (3 H, t, J 7Hz, CH_3), 1.99 (1 H, bs, NH), 3.03 (1H, ddm, J 6Hz, J 14Hz, allylic H), 3.22 (1H, ddm, J 6Hz, J 15Hz, allylic H), 3.79-4.14 (5 H, m, CH_2's and PhCH), 5.08 and 5.13 (1 H, m, $=CH_2$), 5.76-5.90 (1 H, m, -CH=), 7.28-7.43 (5H, m, aromatic H); δ_P{H} (36 MHz, $CDCl_3$) 22.75 ppm; *m/z* (70 eV, 140°C) 283 (M^+, 2), 147 (11), 146 (100), 145 (5), 144 (8), 104 (7), 91 (9) and 41 (18).

Diethyl allylamino(4-methoxyphenyl)methanephosphonate (**28**), yield 96%, m.p. 35°C (Found: C, 57.3; H, 7.8; N, 4.4. $C_{15}H_{24}NO_4P$ requires C, 57.5; H, 7.7; N, 4.5%); $\nu_{max.}$ (film) 2981, 2908, 1610, 1511, 1462, 1304, 1250, 1178, 1098, 1029, 965, 841, 789, 753, 563 and 488 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.16 (3 H, t, J 7Hz, CH_3), 1.28 (3 H, t, J 7Hz, CH_3), 1.83 (1H, bs, NH), 3.01 (1 H, ddm, J 6.5Hz, 14 Hz, allylic H), 3.23 (1 H, ddm, J 5Hz, 14 Hz, allylic H), 3.81 (3 H, s, OCH_3), 3.80-4.13 (5H, m, CH_2's and CH), 5.06-5.14 (2 H, m, $=CH_2$), 5.74-5.89 (1H, m, -CH=), 6.88 (2H, dd, J_{HH} 9 Hz, J_{HP} 1 Hz, aromatic H) and 7.32 (2H, dd, J_{HH} 9 Hz, J_{HP} 2 Hz, aromatic H); δ_P{H} (36MHz, $CDCl_3$) 22.8 ppm; *m/z* (70 eV, 150°C) 313 (M^+, 3), 176 (100), 175 (56), 174 (87), 134 (30), 121 (31), 83 (62), 65 (49) and 41 (52).

Diethyl ^{t}butylamino(4-nitrophenyl)methanephosphonate **(30)**, yield 57%, m.p. 96-97°C (Found: M^+ 344.1501. $C_{15}H_{25}N_2O_5P$ requires 344.1501); $\nu_{max.}$ (nujol) 3311, 1519, 1456, 1365, 1344, 1239, 1108, 1060, 961, 772, 734, and 573 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 0.98 [9H, s, $(CH_3)_3C$], 1.16 (3 H, t, J 7Hz, CH_3), 1.28 (3 H, t, J 7Hz, CH_3), 1.84 (1H, bs, NH), 3.81-4.14 (4H, m, CH_2's), 4.28 (1 H, d, J_{HP} 26 Hz, CH), 7.66 (2H, dd, J_{HH} 9 Hz, J_{HP} 2 Hz, aromatic H) and 8.17 (2H, dd, J_{HH} 9 Hz, J_{HP} 1 Hz, aromatic H), δ_P\{H\} (36 MHz, $CDCl_3$) 22.0 ppm; m/z (70 eV, 100°C) 344 (M^+, 5), 208(12), 207 (100), 191 (24), 152 (7), 151 (81), 105 (11), 57 (36), and 41 (11).

Diethyl (4-nitrophenyl)(phenylamino)methanephosphonate **(32)**, yield 62%, m.p. 150°C (Found: C, 56.0; H, 5.9; N, 7.6. $C_{17}H_{21}N_2O_5P$ requires C, 56.0; H, 5.8; N, 7.7%); $\nu_{max.}$ (nujol) 1603, 1510, 1467, 1347, 1307, 1276, 1234, 1101, 1034, 964, 862, 749, 694 and 589 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.19 (3 H, t, J 7Hz, CH_3), 1.30 (3 H, t, J 7Hz, CH_3), 3.83-4.21 (4 H, m, CH_2's), 4.8-4.9 (2H, m, NH and CH), 6.53 (2H, dm, J 9 Hz, aromatic H), 6.74 (1H, t, 8Hz, aromatic H), 7.12 (2H, ddm, J 9 Hz and 8 Hz, aromatic H), 7.66 (2H, dd, J_{HH} 9 Hz, J_{HP} 2 Hz, aromatic H), 8.20 (2H, dd, J_{HH} 9 Hz, J_{HP} 1Hz, aromatic H); δ_P\{H\} (36 MHz, $CDCl_3$) 20.0 ppm; m/z (70 eV, 150°C) 364 (M^+, 7), 228 (15), 227 (100), 226 (6), 225 (4), 181 (15), 180 (5), 179 (4) and 77 (8).

Diethyl (4-acetamidophenyl)-(4-methoxyphenylamino)methanephosphonate **(36)**, yield 86%, m.p. 157°C (Found: C, 51.3; H, 6.8; N, 6.9. $C_{20}H_{27}N_2O_5P$ requires C, 51.1; H, 6.7; N, 6.9%); $\nu_{max.}$ (nujol) 3352, 3301, 3259, 3192, 3123, 1682, 1604, 1543, 1514, 1321, 1275, 1223, 1054, 1023, 971, 580 and 554 cm^{-1} ; δ_H (270 MHz, $CDCl_3$) 1.14 (3 H, t, J 7Hz, CH_3), 1.29 (3 H, t, J 7Hz, CH_3), 2.16 (3 H, s, $COCH_3$), 3.68 (3 H, s, OCH_3), 3.68-4.18 (4 H, m, CH_2's), 4.65 (1H, d, J_{HP} 24, CH), 6.52 (2H, d, J_{HH} 9 Hz, aromatic H), 6.68 (2H, d, J_{HH} 9 Hz, aromatic H), 7.36 (2H, dd, J_{HH} 8.5 Hz, J_{HP} 2 Hz, aromatic H), 7.47 (2H, d, J_{HH} 8.5 Hz, aromatic H) and 7.65 (1H, bs, NHAc); δ_P\{H\} (36 MHz, $CDCl_3$) 21.8 ppm; m/z (70 eV, 170°C) 406 (M^+, 7), 270 (17), 269 (100), 268 (42), 253 (9), 211 (12), 111 (12), 83 (13), 65 (11) and 43 (9).

Diethyl (4-acetamidophenyl)(phenylamino)methanephosphonate **(38)**, yield 84%, m.p. 151-153°C (Found: C, 60.5; H, 6.7; N, 7.45. $C_{19}H_{25}N_2O_4P$ requires C, 60.6; H, 6.7; N, 7.4%); $\nu_{max.}$ (nujol) 3333, 1677, 1604, 1544, 1509, 1415, 1318, 1282, 1240, 1052, 1026, 975, 753, 570 and 504; δ_H (270 MHz, $CDCl_3$) 1.14 (3 H, t, J 7Hz, CH_3), 1.28 (3 H, t, J 7Hz, CH_3), 2.16 (3 H, s, $CH_3.CO$), 3.68-3.78 and 3.91-4.18 (4 H, m, CH_2's), 4.73 (1H, d, J_{HP} 24, CH), 6.57 (2H, dd, J_{HH} 8.0 Hz, J_{HP} 0.8 Hz, aromatic H), 6.69 (1H, t, 7Hz, aromatic H), 7.10 (2H, d, J_{HH} 8 Hz, J_{HP} 7.5 Hz, aromatic H), 7.385 (2H, d, J_{HH} 9 Hz, J_{HP} 2 Hz, aromatic H), 7.47 (2H, d, J_{HH} 9 Hz, aromatic H) and 7.53 (1H, bs, NHAc); δ_P\{H\} (36 MHz, $CDCl_3$) 21.6 ppm; m/z (70 eV, 160°C) 376 (M^+, 2), 240 (18), 239 (100), 238 (13), 197 (8), 196 (14), 195 (13), 104 (5) and 43 (6).

Diethyl (4-acetamidophenyl)-(4-nitrophenylamino)methanephosphonate **(40)**, yield 74%, m.p. 209-210°C (Found: C, 53.9; H, 5.8; N, 10.05. $C_{19}H_{24}N_3O_6P$ requires C, 54.2; H, 5.7; N, 10.0%); ν_{max} (nujol) 3347, 3256, 3192, 1684, 1601, 1544, 1513, 1330, 1290, 1272, 1234, 1115, 1016, 982 and 576 cm^{-1}; δ_H

(270 MHz, $CDCl_3$) 1.11 (3 H, t, *J* 7Hz, CH_3), 1.29 (3 H, t, *J* 7Hz, CH_3), 2.16 (3 H, s, $COCH_3$), 3.62-3.96 and 4.06-4.20 (4 H, m, CH_2's), 4.79 (1H, dd, J_{HH} 8 Hz, J_{HP} 24, CH), 6.61 (2H, d, J_{HH} 9 Hz, aromatic H), 6.8 (1H, t, 8Hz, ArNH), 7.33 (2H, d, J_{HH} 9 Hz, aromatic H), 7.48 (2H, d, J_{HH} 9 Hz, aromatic H), 7.99 (2H, d, J_{HH} 9 Hz, aromatic H) and 8.37 (1H, bs, NHAc); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 20.1 ppm; *m/z* (70 eV, 160°C) 421 (M^+, 3), 285 (17), 284 (100), 242 (8), 241 (8), 196 (6), 111 (7), 83 (7), 65 (6), and 43 (12).

Benzaldehyde azine adduct (**44**), yield 91%, m.p. 98-100°C (Found: C, 62.1; H, 6.7; N, 7.9. $C_{18}H_{23}N_2O_3P$ requires C, 62.4; H, 6.7; N 8.1%); $\nu_{max.}$ (nujol) 3221, 1494, 1242, 1094, 1058, 1019, 976, 820, 754, 731, 691 and 562 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.13 (3 H, t, *J* 7Hz, CH_3), 1.30 (3 H, t, *J* 7Hz, CH_3), 3.74-4.20 (4 H, m, CH_2's), 4.92 (1H, d, J_{HP} 21 Hz, J_{HH} 7Hz, CH), 6.22 (1 H, bs, NH), 7.23-7.38 and 7.45-7.48 (10H, m, aromatic H) and 7.64 (1 H, s, HC=N); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 20.8 ppm; *m/z* (70 eV, 150°C) 346 (M^+, 5), 210 (16), 209 (100), 208 (7), 131 (9), 106 (9), 104 (11), 91 (8), and 77 (15).

Diethyl hydroxy-(4-nitrophenyl)methanephosphonate (**48**), yield 55%, m.p. 89°C (Found: C, 45.65; H, 5.5; N, 4.8. $C_{11}H_{16}NO_6P$ requires C, 45.7; H, 5.6; N, 4.8%); $\nu_{max.}$ (nujol) 3235, 1598, 1520, 1349, 1263, 1238, 1208, 1160, 1105, 1030, 977, 875, 864, 815, 801, 777, 699 and 559 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.25 (3 H, t, *J* 7Hz, CH_3), 1.28 (3 H, t, *J* 7Hz, CH_3), 4.02-4.16 (4 H, m, CH_2's), 5.16 (1H, dd, J_{HP} 12 J_{HH} 5Hz, CH), 7.66 (2H, d, J_{HH} 8 Hz, J_{HP} 2 Hz, aromatic H) and 8.22 (2H, d, *J* 9 Hz, aromatic H); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 18.9 ppm; *m/z* (70 eV, 120°C) 289 (M^+, 1), 151 (58), 150 (46), 138 (63), 111 (100), 83 (79), 82 (36), 77 (40) and 65 (59).

Diethyl (4-acetamidophenyl)hydroxymethanephosphonate (**49**), yield 88%, m.p. 153-154°C (Found: C, 51.6; H, 6.6; N, 4.7. $C_{13}H_{20}NO_5P$ requires C, 51.8; H, 6.7; N, 4.65%); ν_{max} (nujol) 3310, 1693 (C=O), 1604, 1537, 1511, 1408, 1313, 1275, 1255, 1189, 1059, 1021, 974, 849, 577 and 549 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.21 (3 H, t, *J* 7Hz, CH_3), 1.28 (3 H, t, *J* 7Hz, CH_3), 1.71 (1 H, bs, OH), 2.16 (3 H, s, $COCH_3$), 3.88-4.13 (4 H, m, CH_2's), 4.94 (1H, dd, J_{HP} 12 Hz, J_{HH} 5Hz, CH), 7.34 (2H, d, J_{HH} 8 Hz, J_{HP} 2 Hz, aromatic H), 7.44 (2H, d, *J* 8 Hz, aromatic H) and 8.08 (1H, bs, NHAc); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 20.4 ppm; *m/z* (70 eV, 170°C) 163 (55), 121 (69), 120 (100), 111 (66), 93 (21), 83 (67), 65 (53), 45 (22) and 43 (56).

Diethyl hydroxy-(4-methoxyphenyl)methanephosphonate (**50**), yield 99%, m.p. 116°C (Found: C, 52.4; H, 6.9. $C_{12}H_{19}O_5P$ requires C, 52.55; H, 7.0%); $\nu_{max.}$ (nujol) 3251, 1614, 1586, 1330, 1302, 1251, 1196, 1171, 1108, 1065, 1029, 964, 838, 797, 757, 669, 597 and 558 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.21 (3 H, t, *J* 7Hz, CH_3), 1.27 (3 H, t, *J* 7Hz, CH_3), 3.80 (3 H, s, OCH_3), 3.90-4.10 (4 H, m, CH_2's), 4.05 (1H, d, J_{HP} 12 Hz, J_{HH} 7Hz, CH), 6.89 (2H, d, J_{HH} 8 Hz, aromatic H) and 7.40 (2H, d, *J* 9 Hz, 2 Hz, aromatic H); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 20.9 ppm; *m/z* (70 eV, 100°C) 274 (M^+, 1), 136 (71), 135 (100), 111 (46), 92 (18), 83 (48), 77 (25), 65 (38) and 45 (16).

Diethyl 1,1-bis(ethoxycarbonyl)-1-hydroxymethanephophonate (**51**), yield 76%, oil (Found: C, 42.5; H, 6.8. $C_{11}H_{21}O_8P$ requires C, 42.3; H, 6.8%); $\nu_{max.}$ (film) 2987, 2941, 1752, 1448, 1396, 1372, 1274, 1185, 1123, 1030, 971, 916, 849, 762 and 489 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.30 (6H, t, *J* 7Hz, carboxylate CH_3's), 1.34 (6H, dt, *J* 7Hz, 1 Hz, phosphonate CH_3's), 4.19 (4 H, quartet, carboxylate CH_2's), 4.28 (4H, dquintet, *J* 9 Hz, 3Hz, phosphonate CH_2's) and 5.28 (1H, d, *J* 10 Hz, CH); δ_P{H} (36 MHz, $CDCl_3$) -3.0 ppm; *m/z* (70 eV, 180°C) 312 (M^+, 5), 240 (55), 213 (32), 155 (100), 138 (68), 127 (68), 109 (35), 99 (91), and 81 (45).

Diethyl 1-(ethoxycarbonyl)-1-hydroxyethanephophonate (**52**), yield 20%, oil (Found MH^+ 255.0998. $C_9H_{20}O_6P$ requires 255.0998); $\nu_{max.}$ (film) 3294, 2985, 2938, 1735, 1447, 1393, 1370, 1251, 1152, 1023, 975, 863, 797, 602 and 504 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.30 (3H, t, *J* 7Hz, carboxylate CH_3's), 1.34 (6H, dt, *J* 7Hz, 0.5 Hz, phosphonate CH_3's), 1.6 (3H, d, *J* 16 Hz, 2-Me), 4.11-4.33 (6 H, quartet, carboxylate CH_2's); δ_P{H} (36 MHz, $CDCl_3$) 17.3 ppm; *m/z* (70 eV, 140°C) 111 (86), 93 (28), 83 (100), 81 (27), 67 (26), 65 (70), 45 (35) and 43 (93); *m/z* (CI/NH_3) 255 (MH^+, 100).

Diethyl 1-(4-nitrophenylamino)-3-phenylprop-2-enephosphonate (**54**), yield 70%, m.p. 104°C (Found: C, 58.45; H, 5.9; N, 7.1. $C_{19}H_{23}N_2O_5P$ requires C, 58.5; H, 5.9; N, 7.2%); $\nu_{max.}$ (nujol) 3237, 1599, 1552, 1307, 1228, 1183, 1113, 1047, 1024, 963, 834, 757, 725, 695 and 562 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.31 (3 H, t, *J* 7Hz, CH_3), 1.33 (3 H, t, *J* 7Hz, CH_3), 4.08-4.26 (4 H, m, CH_2's), 4.53 (1H, ddd, *J* 25 Hz, 8 Hz, 6 Hz, H-1), 4.53 (1H, dd, *J* 16 Hz, 8 Hz, H-3), 6.23 (1H, dd, *J* 16 Hz, 6 Hz, H-2), 6.67 (2H, d, *J* 9 Hz, aromatic H), 7.25-7.36 (5H, m, aromatic H), 8.09 (2H, d, *J* 9 Hz, aromatic H); δ_P{H} (36 MHz, $CDCl_3$) 20.2 ppm; *m/z* (70 eV, 150°C) 390 (M^+, 11), 254 (17), 253 (100), 251 (15), 205 (7), 130 (8), 115 (9), 84 (6) and 49 (9).

Diethyl 3-phenyl-1-(phenylamino)prop-2-enephosphonate (**56**), yield 91%, m.p. 87°C (Found: C, 65.9; H, 7.2; N, 4.1. $C_{19}H_{24}NO_3P$ requires C, 66.1; H, 7.0; N, 4.1%); $\nu_{max.}$ (film) 3300, 2982, 1603, 1499, 1236, 1098, 1053, 1024, 970, 751, 694 and 547 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.26 (3 H, t, *J* 7Hz, CH_3), 1.28 (3 H, t, *J* 7Hz, CH_3), 4.07-4.22 (4 H, m, CH_2's), 4.35 (1H, m, H-1), 6.25 (1H, ddd, *J* 25 Hz, 6 Hz, 5 Hz, vinylic H-2), 6.65-6.75 and 7.10-7.35 (11H, m, aromatic H and vinylic H-3); δ_P{H} (36 MHz, $CDCl_3$) 21.5 ppm; *m/z* (70 eV, 100°C) 345 (M^+, 9), 209 (17), 208 (100), 207 (6), 206 (15), 115 (8), 91 (4), 77 (8) and 43 (14).

Diethyl 1-(4-methoxyphenylamino)-3-phenylprop-2-enephosphonate (**58**), yield 77%, m.p. 98°C (Found: C, 64.0; H, 7.0; N, 3.8. $C_{20}H_{26}NO_4P$ requires C, 64.0; H, 7.0; N, 3.7%); $\nu_{max.}$ (nujol) 3290, 1527, 1506, 1265, 1225, 1161, 1042, 1016, 970, 943, 818 and 749 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.30 (6 H, t, *J* 7Hz, CH_3's), 1.63 (1H, bs, NH), 3.73 (3H, s, OCH_3), 4.08-4.24 (4 H, m, CH_2's), 4.38 (1H, dd, *J* 25 Hz, 7Hz, allylic H-1), 6.25 (1H, ddd, *J* 16 Hz, 6 Hz, 5 Hz, vinylic H-2), 6.66 (2H, d, *J* 9 Hz, aromatic H), 6.73 (1H, overlapping ddd, vinylic H-3), 6.77 (2H, d, *J* 9 Hz, aromatic H), 7.22-7.37 (5H, m, aromatic H); δ_P{H} (36 MHz, $CDCl_3$) 21.8 ppm; *m/z* (70 eV, 120°C) 375 (M^+, 7), 239 (11), 238 (66), 237 (59), 236 (100), 115 (23), 111 (18), 83 (17) and 65 (12).

Diethyl 1-(4-phenylamino)but-2-enephosphonate **(60)**, yield 54%, m.p. 48°C (Found: C, 59.4; H, 7.9; N, 4.9. $C_{14}H_{22}NO_3P$ requires C, 59.35; H, 7.8; N, 4.9%); $\nu_{max.}$ (nujol) 3292, 1602, 1532, 1499, 1306, 1235, 1155, 1058, 1029, 966, 803, 746, 691 and 590 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.27 (3 H, t, *J* 7Hz, CH_3), 1.31 (3 H, t, *J* 7Hz, CH_3), 1.71 (3 H, apparent t, *J* 6Hz, $C{=}CCH_3$), 4.07-4.32 (5H, m, CH_2's and CH), 5.46-5.86 (1H, m, H-3), 5.74-5.86 (1H, m, H-2), 6.64 (2H, d, *J* 8 Hz, aromatic H), 6.72 (1H, t, *J* 7 Hz, aromatic H), 7.16 (2H, dd, *J* 9 Hz, 8Hz, aromatic H); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 22.4 ppm; *m/z* (70 eV, 160°C) 283 (M^+, 5), 149 (40), 147 (11), 146 (100), 145 (19), 144 (23), 111 (10), 83 (11) and 77 (21).

Diethyl 1-(4-methoxyphenylamino)but-2-enephosphonate **(62)**, yield 57%, oil (Found: C, 57.2; H, 7.7; N, 4.7. $C_{15}H_{24}NO_4P$ requires C, 57.5; H, 7.7; N, 4.5%); $\nu_{max.}$ (film) 3304, 2983, 2833, 1619, 1511, 1443, 1392, 1237, 1179, 1097, 1028, 969, 823, 793 and 510 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.28 (3 H, t, *J* 7 Hz, 0.5 Hz, CH_3), 1.31 (3 H, t, *J* 7Hz, 0.5 Hz, CH_3), 1.71 (3 H, tm, *J* 5 Hz, $CH_3{=}C$), 3.73 (3 H, s, OCH_3), 4.08-4.22 (5 H, m, CH_2's and CH), 5.44-5.54 (1H, m, H-3), 5.74-5.84 (1H, m, H-2), 6.61 (2H, d, *J* 9 Hz, aromatic H), 6.76 (2H, d, *J* 9 Hz, aromatic H); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 22.6 ppm; *m/z* (70 eV, 120°C) 313 (M^+, 10), 177 (12), 176 (100), 175 (21), 160 (14), 111 (31), 83 (27) and 65 (19).

Diethyl (N-phenylcarbamoyl)phosphonate **(63)**, yield 87%, oil (Found: C, 51.3; H, 6.3; N, 5.4. $C_{11}H_{16}NO_4P$ requires C, 51.4; H, 6.3; N, 5.5%); $\nu_{max.}$ (nujol) 3240, 2985, 1662, 1601, 1542, 1499, 1445, 1319, 1264, 1228, 1164, 1025, 980, 800, 758, 693, and 537 cm^{-1}; δ_H (2 '0 MHz, $CDCl_3$) 1.40 (6 H, t, *J* 7Hz, CH_3's), 4.19-4.39 (4 H, m, CH_2's), 7.18 (1H, t, *J* 7.5Hz, aromatic H), 7.33 (2H, d, *J* 7.5 Hz, aromatic H), 7.66 (2H, d, *J* 7.5 Hz, aromatic H) and 9.07 (1H, bs, NH); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) -2.6 ppm; *m/z* (70 eV, 140°C) 257 (M^+, 18), 138 (100), 111 (75), 110 (21), 109 (18), 83 (25), 82 (50) and 65 (16).

Diethyl (N-4-nitrophenylcarbamoyl)phosphonate **(64)**, yield 86%, m.p. 142°C (Found: C, 43.7; H, 4.8; N, 9.3. $C_{11}H_{15}N_2O_6P$ requires C, 43.7; H, 5.0; N, 9.3%); $\nu_{max.}$ (nujol) 3199, 1677, 1597, 1556, 1505, 1338, 1305, 1263, 1228, 1180, 1111, 1049, 1028, 986, 957, 861, 754, 652, and 571 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.43 (6 H, t, *J* 7Hz, CH_3's), 4.25-4.40 (4 H, m, CH_2's), 7.97 (2H, d, *J* 9 Hz, aromatic H), 8.24 (2H, d, *J* 9 Hz, aromatic H) and 10.12 (1H, bs, NH); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) -4.2 ppm; *m/z* (70 eV, 140°C) 302 (M^+, 14), 138 (100), 111 (74), 109 (43), 91 (28), 84 (36), 83 (45), 82 (36) and 65 (31).

Diethyl 4-methylphenylamino-(4-methylphenylimino)methanephosphonate **(66)** yield 76%, m.p. 88°C (Found: C, 63.1; H, 7.0; N, 7.7. $C_{19}H_{25}N_2O_3P$ requires C, 63.3; H, 7.0; N 7.8%); $\nu_{max.}$ (nujol) 3283, 1596, 1505, 1316, 1251, 1163, 1109, 1028, 967, 923, 822, 768, 735, 683, 646, 602, 553 and 504 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.22 (6 H, bt, *J* 7Hz, CH_3's), 2.30 (6 H, t, *J* 7Hz, $ArCH_3$'s), 3.96 (4 H, bm, CH_2's), 6.75-6.8 (2H, bm, aromatic H), 7.04-7.62 (4H, bm, aromatic H), 7.6-7.62 (2H, bm, aromatic H), 7.77-7.78 (1 H, bs, NH); $\delta_P\{H\}$ (36 MHz, $CDCl_3$) 3.1 ppm; *m/z* (70 eV, 160°C) 360 (M^+, 43), 255 (14), 254 (100), 223 (13), 222 (16), 198 (12), 118 (20), 109 (9) and 91 (19).

Acknowledgement

We thank BP International Ltd. for a studentship to K.A.

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