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Organophosphorus Chemistry. IV* Synthesis and Reactions of 2-Ethoxy-6-oxo-1,2-azaphosphinane 2-Oxide

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Abstract

2-Ethoxy-6-oxo-1,2-azaphosphinane 2-oxide (3) has been prepared by cyclocondensation of ethyl 4-(*P*-amino-*P*-ethoxyphosphinoyl)butanoate (17). *N*-Alkylated derivatives of (3) were prepared by cyclocondensation of (17) in the presence of methyl iodide, allyl bromide and benzyl chloride. These derivatives reacted with organometallic reagents and bases to yield acyclic products.

Introduction

Our search for biologically active analogues of anabasine (1) required the synthesis of aryl substituted 1,2-azaphosphinanes such as (2). A potential intermediate in this synthesis was 2-ethoxy-6-oxo-1,2-azaphosphinane 2-oxide (3). Several 1,2-azaphosphinanes (4) have been prepared by the intramolecular base catalysed dehydrohalogenation of haloalkyl phosphonamidates.[1,2] This method is unsuitable for our purposes because a carbonyl group cannot easily be introduced into the 6 position of the ring.

Khairullin *et al.*[3] and Pudovik *et al.*[4] have prepared related compounds which have a five-membered ring. They condensed primary amines with 3-chloroformylpropylphosphinoyl chlorides (5) in the presence of triethylamine to yield substituted 1,2-azaphospholanes (6). This procedure could easily be modified to our needs and it would produce *N*-protected 1,2-azaphosphinanes ready for reactions with organometallic reagents such as pyridin-3-yllithium. Attaching the 3-pyridinyl group to *N*-protected lactams is not a well recognized reaction but Lukes and Cervinka[5] have used it to synthesize DL-nicotine (7) from *N*-methylpyrrolidin-4-one and pyridin-3-yllithium.

* Part III, *Aust. J. Chem.*, 1984, **37**, 205.

[1] Helferich, B., and Curtius, U., *Justus Liebigs Ann. Chem.*, 1962, **655**, 59.
[2] Hewitt, D. G., and Newland, G. L., *Aust. J. Chem.*, 1977, **30**, 579.
[3] Khairullin, V. K., Kondrat'eva, R. M., and Pudovik, A. N., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, **6**, 1375.
[4] Pudovik, A. N., Kondrat'eva, R. M., and Khairullin, V. K., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, **9**, 2076.
[5] Lukes, R., and Cervinka, O., *Collect. Czech. Chem. Commun.*, 1961, **26**, 1893.

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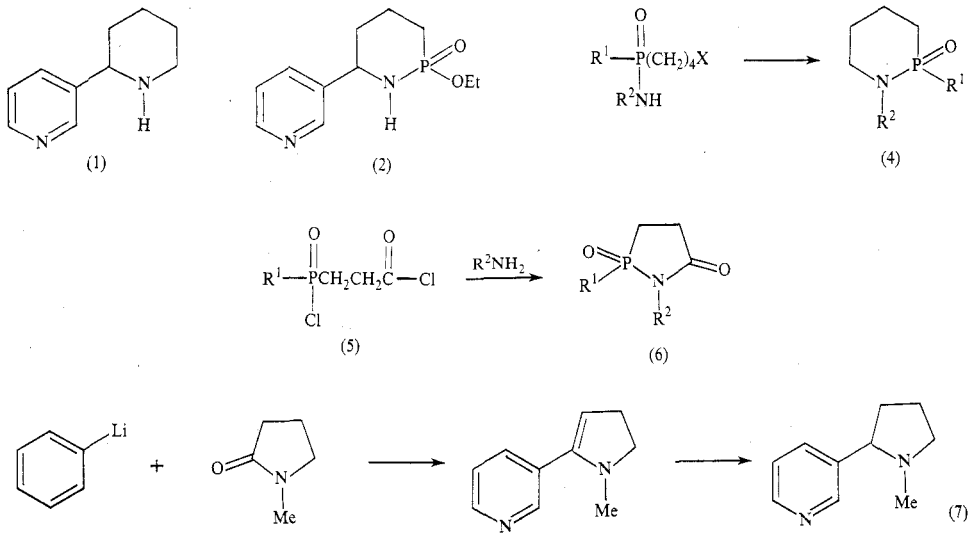
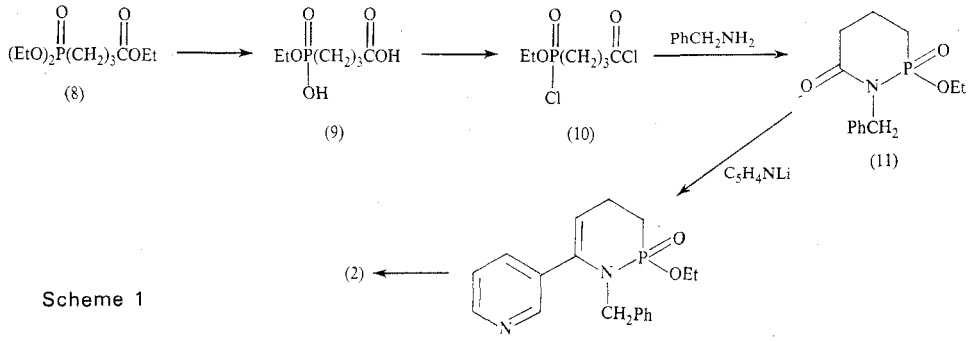


Discussion

By adapting the method of Khairullin[3] the route shown in Scheme 1 to aryl substituted 1,2-azaphosphinanes (2) was proposed. Benzylamine was chosen to react with 4-(*P*-chloro-*P*-ethoxyphosphinoyl)butyryl chloride (10) because the benzyl protecting group can be easily hydrogenolysed. Allylamine is also suitable for this purpose.



Scheme 1

Some difficulty was expected in selectively hydrolysing one *P*-ester and one *C*-ester in ethyl 4-(diethoxyphosphinoyl)butanoate (8) to 4-(ethoxyphosphinoyl)butanoic acid (9). The carboxylic acid ester group in (8) can be selectively removed by alcoholic potassium hydroxide.[6] The two phosphorus ester groups in (8) can be removed by dealkylation with lithium iodide and chlorotrimethylsilane.[7] All three ester groups in (8) can be removed by treatment with concentrated acid.[8,9] Acid or base hydrolysis of

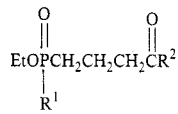
[6] Tsvetkov, E. N., Malevannaya, R. A., and Kabachnik, M. I., *Zh. Obshch. Khim.*, 1975, **45**, 706.
[7] Machida, Y., Nomoto, S., and Saito, I., *Synth. Commun.*, 1979, **9**, 97.
[8] Kreutzkamp, N., and Mengel, W., *Arch. Pharm. (Weinheim, Ger.)*, 1962, **295**, 773.
[9] Nylen, P., *Ber. Dtsch. Chem. Ges.*, 1926, **59**, 1119.

the closely related ethyl 3-(diethoxyphosphinoyl)propanoate (12) selectively cleaved one phosphorus and one carboxylic acid ester and it was found that the remaining *P*-ester group was extremely difficult to cleave[9] (Scheme 2).

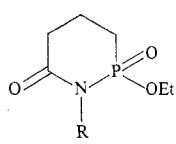
(12)

Scheme 2

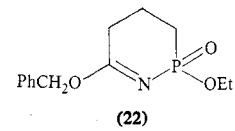
An investigation of hydrolysis reactions of ethyl 4-(diethoxyphosphinoyl)butanoate[10] (8) has shown that one, two or three ester groups can be cleaved selectively, in an order which depends upon the reagents and reaction conditions used. It was found that boiling the ester (8) in water containing a catalytic amount of *p*-toluenesulfonic acid (TsOH) for 24 h selectively hydrolysed the carboxylate ester in high yield (75%) to yield the carboxylic acid (13).



	R^1	R^2		R^1	R^2
(8)	OEt	OEt	(18)	NHMe	OEt
(9)	OH	OH	(23)	Ph	$NHCH_2CH{=}CH_2$
(10)	Cl	Cl	(24)	OEt	$NHCH_2CH{=}CH_2$
(13)	OEt	OH	(25)	$OCH_2CH{=}CH_2$	$NHCH_2CH{=}CH_2$
(14)	OH	OEt	(26)	Ph	NHMe
(15)	Cl	OEt	(27)	OEt	NHMe
(16)	$NHCH_2Ph$	OEt	(28)	OEt	$N(Et)CH_2CH{=}CH_2$
(17)	NH_2	OEt	(29)	$OCH_2CH{=}CH_2$	$N(Et)CH_2CH{=}CH_2$



(3) R = H
(11) R = CH_2Ph
(19) R = Me
(21) R = $CH_2CH{=}CH_2$
(30) R = Et



(22)

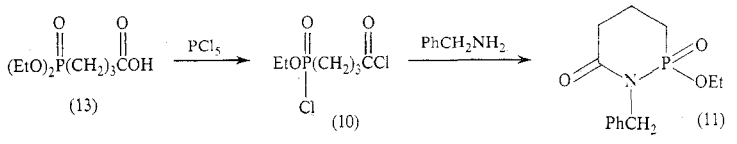
When the ester (8) was treated with refluxing alcoholic sodium hydroxide for 24 h, 4-(ethoxyphosphinoyl)butanoic acid (9) was formed in 84% yield. The second phosphonic ester group was not attacked under these conditions.

The ^1H n.m.r. of (9) showed that only one phosphonic ethyl ester was present. Attempts to purify the acid (9) by distillation led to significant anhydride formation and it did not precipitate a metal salt upon treatment with silver nitrate or lead acetate solution. The identity of the acid was supported by its potentiometric titration curve which showed the presence of a phosphonic acid [inflexion at pH 2·5; lit.[11] pK_a 2 for EtP(O)(OEt)(OH)] and a carboxylic acid group (inflexion at pH 9). The neutralization equivalent was found to be 93·5 g/equiv. (theoretical 98 g/equiv.). G.c.–m.s. analysis caused (9) to decarboxylate in the gas chromatograph to form ethyl propylphosphonic acid. A trace amount of 4-(diethoxyphosphinoyl)butanoic acid (13) was also present.

[10] Falbe, J., Paatz, R., and Korte, F., *Chem. Ber.*, 1965, **98**, 2312.
[11] Van Wazer, J. R., 'Phosphorus and its Compounds' Vol. 1, p. 350 (Interscience: New York 1958).

Treating the acid (9) with thionyl chloride gave black tars from which no diacid chloride could be isolated. When benzylamine was added to the crude mixture only very small quantities of benzyl-containing products were formed so the procedure was abandoned.

The carboxylic acid (13) is easier to prepare than the diacid (9) and it was converted into the diacid chloride (10) in high yield (90%) by treatment with two molar proportions of phosphorus pentachloride in carbon tetrachloride at 40° (Scheme 3).

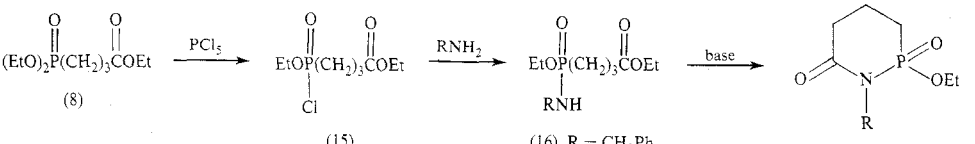


(13) (10) (11)

Scheme 3

Equimolar quantities of freshly distilled benzylamine and triethylamine were mixed and then added dropwise to the diacid chloride (10) in tetrahydrofuran at 0°. A fast exothermic reaction occurred but inconsistent and very low yields (<18%) of crude 1-benzyl-2-ethoxy-6-oxo-1,2-azaphosphinane 2-oxide (11) were obtained. The reaction was repeated using benzene and dimethylformamide at various temperatures between −70° and 0°, but consistently poor results were obtained. Attempted purification of crude 1-benzyl-2-ethoxy-6-oxo-1,2-azaphosphinane 2-oxide (11) by distillation produced extensive decomposition and impure product.

A better method for synthesizing 1-benzyl-2-ethoxy-6-oxo-1,2-azaphosphinane 2-oxide (11) was needed. The reaction above was split into two separate reactions to provide a less vigorous, more controlled cyclization process as depicted in Scheme 4.



(8) (15) (16) R = CH_2Ph (17) R = H (18) R = Me (3) R = H (19) R = Me

Scheme 4

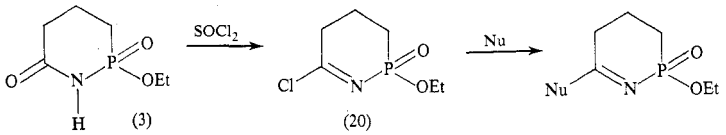
Ethyl 4-(*P*-chloro-*P*-ethoxyphosphinoyl)butanoate (15) was prepared in high yield (80%) from ethyl 4-(diethoxyphosphinoyl)butanoate (8) and one mole of phosphorus pentachloride. The acid chloride (15) was then treated with benzylamine and triethylamine in tetrahydrofuran at 0°. This reaction gave a fair yield (*c.* 50%) of ethyl 4-(*P*-benzylamino-*P*-ethoxyphosphinoyl)butanoate (16); however, attempts to purify this substance caused decomposition to occur.

When ethyl 4-(*P*-chloro-*P*-ethoxyphosphinoyl)butanoate (15) was added to ice-cold 30% aqueous ammonia the expected product, ethyl 4-(*P*-amino-*P*-ethoxyphosphinoyl)butanoate (17), formed in 78% yield. This substance was isolated as a white crystalline solid which had a sharp melting point and displayed the expected spectroscopic properties. When aqueous methylamine was used in place of ammonia the expected *N*-methyl compound ethyl 4-(*P*-ethoxy-*P*-methylaminophosphinoyl)-butanoate (18) was obtained but in much lower yield (20%). When compound (17) was treated with sodium hydride in benzene cyclocondensation proceeded to give 2-ethoxy-6-oxo-1,2-azaphosphinane 2-oxide (3) in 50% yield. It was found that

cyclization could be achieved more conveniently by use of potassium t-butoxide in t-butyl alcohol. The *N*-methyl compound (18) also cyclized upon treatment with potassium t-butoxide in t-butyl alcohol to give a very low yield (< 10%) of 2-ethoxy-1-methyl-6-oxo-1,2-azaphosphinane 2-oxide (19).

The poor yield associated with the *N*-methyl series of compounds forced us to discard this route as a viable pathway to synthesize *N*-protected 1,2-azaphosphinanes. The *N*-allyl and *N*-benzyl compounds would be expected to form in low yield, so it was decided to concentrate on methods which would transform 2-ethoxy-6-oxo-1,2-azaphosphinane 2-oxide (3) into aryl-substituted 1,2-azaphosphinanes.

The most direct method for achieving this aim involves preparing the imidoyl chloride derivative (20) of (3). The imidoyl chloride (20) would be expected to undergo substitution reactions with nucleophiles to yield substituted 1,2-azaphosphinanes as shown in Scheme 5.



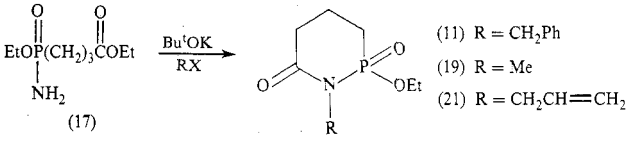
(3) (20)

Scheme 5

Imidoyl chlorides are unstable species and are not often isolated because they break down to nitriles and alkyl halides upon heating. This is particularly so when the group adjacent to nitrogen is prone to attack by nucleophiles.[12]

The 1,2-azaphosphinane (3) and thionyl chloride in benzene did not react at room temperature. Heating to 70° caused acidic gases to evolve and the mixture turned black. Infrared analysis of the mixture showed an absorbance at 2240 cm^{-1} indicating that a nitrile had formed. Attempts to isolate the products from this reaction led to extensive decomposition and charring of the mixture. This messy and unpleasant procedure was abandoned and attention focused on synthetic routes which utilize *N*-protected 1,2-azaphosphinanes as intermediates.

One such intermediate, 2-ethoxy-6-oxo-1-(prop-2′-enyl)-1,2-azaphosphinane 2-oxide (21), was conveniently prepared in 50% yield by the base-catalysed alkylation of 2-ethoxy-6-oxo-1,2-azaphosphinane 2-oxide (3) with allyl bromide. The best base and solvent for this process was potassium t-butoxide and t-butyl alcohol. When it was discovered that the cyclization and alkylation reactions proceeded well in the same reaction medium (potassium t-butoxide/t-butyl alcohol) the two reactions were combined into one. This resulted in doubling (to 50%) the overall yield for conversion of ethyl 4-(*P*-amino-*P*-ethoxyphosphinoyl)butanoate (17) into 2-ethoxy-6-oxo-1-(2′-propenyl)-1,2-azaphosphinane 2-oxide (21). This method also gave a good yield (57%) of the *N*-methyl-protected compound 2-ethoxy-1-methyl-6-oxo-1,2-azaphosphinane 2-oxide (19). The *N*-benzyl compound 1-benzyl-2-ethoxy-6-oxo-1,2-azaphosphinane 2-oxide (11) was also synthesized but in lower yield (26%).



(17)

(11) R = CH_2Ph
(19) R = Me
(21) R = $CH_2CH{=}CH_2$

Scheme 6

[12] Vaughan, W. R., and Carlson, R. D., *J. Am. Chem. Soc.*, 1962, **84**, 769.

An isomer of (11) 6-benzyloxy-2-ethoxy-2,3,4,5-tetrahydro-1,2-azaphosphinine 2-oxide (22) also formed in 12% yield along with 9% of the intermediate (3) (Scheme 6). When benzyl bromide was used as the alkylating agent, the yield of *N*-benzyl isomer (11) doubled and the yield of *O*-benzyl isomer (22) decreased marginally (13% to 11%), but only trace amounts of intermediate (3) were found.

It is interesting to note that *N*- and *O*-isomers were only found when benzyl chloride or bromide was used as the alkylating agent. This seems to indicate that benzyl halides, being harder electrophiles than methyl iodide and allyl bromide,[13] interact more with the hard oxygen end of the resonance stabilized anionic reaction intermediate. Gas chromatography by means of packed or capillary columns showed no trace of *O*-allyl or *O*-methyl isomers. However, the *N*- and *O*-benzyl isomers were easily separated on a packed column. Their presence could also be detected in the ^{1}H n.m.r. with the benzylic methylene in (22) appearing as a singlet at δ 5·22 while the benzylic methylene in (11) appeared as a multiplet at 4·75. The ratio of *O*- to *N*-benzyl isomers was established by ^{1}H n.m.r. as well as g.c.–m.s. data.

The complete removal of compound (3) from (11) and (22) was difficult and g.c.–m.s. was used to provide evidence for structures (11) and (22). Both isomers showed molecular ions at *m/z* 267 but their fragmentation patterns were considerably different. The fragmentation pattern of (22) featured the loss of benzaldehyde to give an intense fragment at *m/z* 161. Compound (11) degraded to give a more complex fragmentation pattern.

Phenyllithium and phenylmagnesium bromide were expected to attack 2-ethoxy-6-oxo-1-(prop-2′-enyl)-1,2-azaphosphinane 2-oxide (21) at either the carbonyl group or the phosphoryl group. Either process could give cyclic and/or acyclic products. Acyclic products could form more easily here than from simple lactams with organometallic reagents because the carbonyl and phosphoryl groups make nitrogen a better leaving group. However, previous work[2] has shown that replacement of ethoxide or ring opening by attack at phosphorus in similar compounds lacking the ring carbonyl is extremely difficult and we thought it unlikely to occur in this reaction. But the carbonyl group adjacent to nitrogen in (21) increases the likelihood of ring opening and could cause some P–N cleavage. Substitution of the ethoxide group by phenyl should not occur because pseudorotation of the transition state is hindered.[14]

The reaction did not proceed as expected but instead gave low yields (*c.* 20%) of three products derived from nucleophilic attack at phosphorus. Traces of starting material (21) were present but the major substance formed was a high-melting (>300°) probably polymeric solid which contained no phenyl groups (Scheme 7).

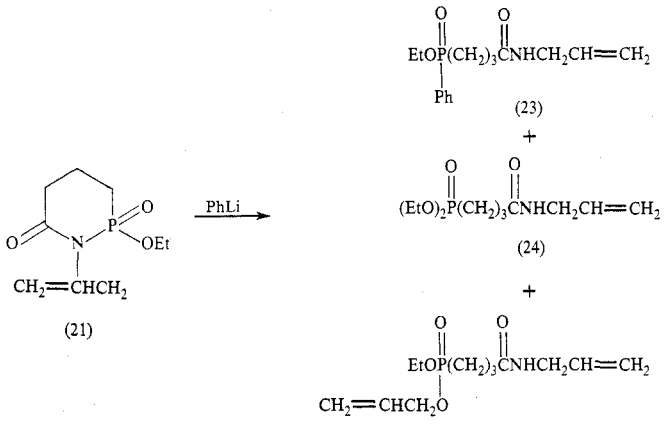
Since none of the desired products had formed, compounds (23), (24) and (25) were not fully characterized and their structures were deduced from g.c.–m.s., infrared and ^{1}H n.m.r. data. Compounds (23) and (24) formed in about 4·6% and 4·7% yield respectively. Compound (25) formed in only 0·9% yield.

Compound (23) 4-(*P*-ethoxy-*P*-phenylphosphinoyl)-*N*-(prop-2′-enyl)butanamide was isolated as a white solid m.p. 98–102°. The infrared spectrum of (23) shows a N–H stretch at 3230 cm^{-1} and a strong carbonyl stretch at 1655 cm^{-1} indicating the carboxamide functional group. The ^{1}H n.m.r. of (23) supported the proposed

[13] Fleming, I., 'Frontier Orbitals and Organic Chemical Reactions' p. 35 (Wiley–Interscience: New York 1976).
[14] Westheimer, F. H., *Acc. Chem. Res.*, 1968, **1**, 70.

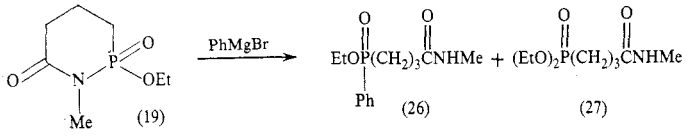
structure. The mass spectrum of (23) displayed the correct molecular ion peak at *m/z* 295 and an appropriate fragmentation pattern.

Compounds (24) and (25) were not isolated in a pure state. However, g.c.–m.s. analysis of this mixture showed that each had the correct molecular ion peak and a fragmentation pattern which correlated with the proposed structures. In addition, (23), (24) and (25) underwent the same systematic degradation process in the mass spectrometer indicating that all three compounds had similar structural features.

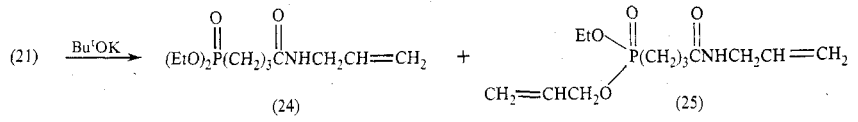


Scheme 7

The reaction of phenylmagnesium bromide with 2-ethoxy-1-methyl-6-oxo-1,2-azaphosphinane 2-oxide (19) followed a course similar to (21) (Scheme 8). Analysis showed that phenyl- and ethoxyl-substituted products (26) and (27) had formed along with a large amount of presumably polymeric solid but no other products were detected.



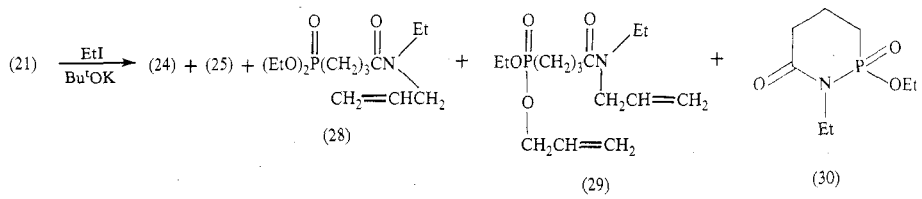
Scheme 8



Scheme 9

The formation of (23) and (26), although unexpected, can be explained by direct nucleophilic attack of phenyllithium or phenylmagnesium bromide upon the phosphorus atom of (21) and (19) respectively. The formation of (24), (25) and (27) has not been investigated in detail but some interesting preliminary observations have been made. When (21) was treated with potassium t-butoxide in t-butyl alcohol compounds (24) and (25) formed indicating the reaction to be base catalysed (Scheme 9). When (21) was treated with t-butoxide and ethyl iodide in t-butyl alcohol compounds (24) and (25) formed along with their *N*-ethyl derivatives, compounds (28) and (29) respectively. In addition, 2-ethoxy-1-ethyl-6-oxo-1,2-azaphosphinane

2-oxide (30) also formed (Scheme 10). The formation of (30) suggests that the *N*-anion of (3) could be an intermediate formed from (21) in the presence of base. Hence (21) may be undergoing base-catalysed intermolecular alkyl transfer processes in these reactions.



Scheme 10

Experimental

Melting and boiling points are uncorrected. Infrared spectra were recorded with a Perkin–Elmer 710-B infrared spectrometer and ^{1}H n.m.r. with a Perkin–Elmer R12-B spectrometer operating at 60 MHz. Chemical shifts are in ppm from tetramethylsilane. Coupling constants (*J*, in Hz) are measured from first-order considerations only. Mass spectra and g.c.–m.s. data were recorded at 70 eV on a Jeol JMF DX300 mass spectrometer using a BP-1 column (0·2 mm by 25 m). Gas chromatography was carried out on Moduline 2800 GC with a 5%-SE30 column (3·2 mm by 1·8 m) and a temperature program; 230° (4 min), 20°/min to 270°. Microanalyses were carried out by AMDEL, Melbourne.

4-(Diethoxyphosphinoyl)butanoic Acid (13)

Ethyl 4-(diethoxyphosphinoyl)butanoate[10] (8) (20 g, 0·079 mol) was dissolved in water (200 ml) and refluxed with a catalytic amount of *p*-toluenesulfonic acid for 24 h. The solvent was removed and the residual oil distilled to give pure 4-(diethoxyphosphinoyl)butanoic acid (13) (13·3 g, 75%), b.p. 140–145°/0·03 mm (lit.[6] m.p. 45–46°) (Found: C, 42·7; H, 7·6; P, 13·8. Calc. for $C_8H_{17}O_5P$: C, 42·9; H, 7·6; P, 13·8). ^{1}H n.m.r. δ ($CDCl_3$) 1·33, t, *J* 7 Hz, 6H $2\times CH_3CH_2O$; 1·6–2·6, m, $CH_2CH_2CH_2$; 4·17, quintet (dq), *J* 7 Hz, 4H $2\times OCH_2CH_3$; 10·78, s, OH. Adding D_2O removed this peak. ν_{max} (film) 3000 (broad OH), 2990, 1720, 1200, 1020, 960, 780 cm^{-1}. Mass spectrum *m/z* 207 (57%), 180 (11), 179 (62), 178 (14), 165 (100), 152 (89), 151 (13), 138 (39), 137 (22), 125 (62), 123 (60), 111 (28), 109 (39), 108 (17), 105 (12), 97 (29), 96 (11), 82 (15), 81 (29), 80 (11), 65 (19), 45 (12), 42 (24), 41 (34), 29 (40), 27 (21).

4-(Ethoxyphosphinoyl)butanoic Acid (9)

Ethyl 4-(diethoxyphosphinoyl)butanoate (8) (5 g, 0·02 mol) and sodium hydroxide (2 g, 0·05 mol) were dissolved in ethanol (30 ml) and water (6 ml). The mixture was refluxed for 24 h. The solvent was evaporated and the residue dissolved in water and acidified with hydrochloric acid. The mixture was evaporated and the residue extracted with acetone. Evaporation of the extracts gave crude 4-(ethoxyphosphinoyl)butanoic acid (9) (3·3 g, 84%). Distillation of this acid gave a mixture of acids and anhydrides. The neutralization equivalent of this sample 93·5 g/equiv. agreed with that expected for 4-(ethoxyphosphinoyl)butanoic acid (9) 98 g/equiv. The crude acid (9) did not precipitate a silver, lead or anilinium salt. ^{1}H n.m.r. internal standard was sodium 3-(trimethylsilyl)propylsulfonate. δ (D_2O) 1·34, t, *J* 7 Hz, CH_3CH_2O; 1·6–2·4, m, CH_2CH_2P; 2·53, t, *J* 7 Hz, CH_2CO_2; 4·13, dq, *J* 7 Hz, $POCH_2CH_3$. G.c.–m.s. analysis caused (9) to decarboxylate and form ethyl propylphosphonic acid. Mass spectrum 151 (M, 55%), 150 (17), 133 (14), 123 (13), 122 (18), 106 (26), 105 (14), 96 (11), 78 (17), 70 (18), 65 (17), 47 (11), 42 (100), 41 (35), 39 (23), 29 (13), 27 (23).

4-(P-Chloro-P-ethoxyphosphinoyl)butyryl Chloride (10)

Phosphorus pentachloride (56 g, 0·27 mol) was added in small portions to 4-(diethoxyphosphinoyl)butanoic acid (13) (30 g, 0·135 mol) in carbon tetrachloride (300 ml) over 5 h at 40°. The

mixture was stirred overnight at 40°. The mixture was evaporated and distilled to give *4*-(P-*chloro*-P-*ethoxyphosphinoyl*)*butyryl chloride* (10) (23·9 g, 76%), b.p. 121°/0·15 mm (Found: C, 30·5; H, 4·9; P, 12·9. $C_6H_{11}Cl_2O_3P$ requires C, 30·9; H, 4·8; P, 13·3). ^{1}H n.m.r. δ (CCl_4) 1·43, t, *J* 7 Hz, CH_3CH_2OP; 1·6–2·7, m, PCH_2CH_2; 3·13, t, *J* 7 Hz, CH_2COCl; 4·3, m, $POCH_2CH_3$. ν_{max} (film) 2960, 2900, 1795, 1265, 1030, 965 cm^{-1}.

Ethyl 4-(P-*Chloro*-P-*ethoxyphosphinoyl*)*butanoate* (*15*)

Phosphorus pentachloride (41·3 g, 0·2 mol) was added in small portions to ethyl 4-(diethoxyphosphinoyl)butanoate (8) (50 g, 0·2 mol) in carbon tetrachloride (500 ml) over 3 h at 40°. The mixture was stirred overnight at 40°. The mixture was evaporated and distilled to give *ethyl 4*-(P-*chloro*-P-*ethoxyphosphinoyl*)*butanoate* (15) (39·7 g, 81%), b.p. 118°/0·1 mm (Found: C, 39·1; H, 6·8; P, 12·9. $C_8H_{16}ClO_4P$ requires C, 39·6; H, 6·7; P, 12·8). ^{1}H n.m.r. δ (CCl_4) 1·26, t, *J* 7 Hz, $CO_2CH_2CH_3$; 1·32, t, *J* 7 Hz, $POCH_2CH_3$; 1·7–2·7, m, $PCH_2CH_2CH_2$; 4·2, m, $POCH_2 + CO_2CH_2$. ν_{max} (film) 2960, 1735, 1260, 1200, 1025, 960 cm^{-1}. Mass spectrum 242 (M, <10%), 207 (100), 206 (19), 193 (17), 179 (30), 151 (23), 123 (13), 58 (14).

Ethyl 4-(P-*Amino*-P-*ethoxyphosphinoyl*)*butanoate* (*17*)

Ethyl 4-(*P*-chloro-*P*-ethoxyphosphinoyl)butanoate (15) (10 g, 0·0413 mol) was added dropwise with shaking to 30% aqueous ammonia (30 ml) at 0°. When the addition was complete the mixture was stirred for an additional hour and allowed to reach room temperature. The mixture was thoroughly extracted with chloroform (4 × 15 ml) and the extracts dried over anhydrous sodium sulfate. The solvent was removed to leave an oil which readily crystallized. Recrystallization from benzene/pentane gave *ethyl 4*-(P-*amino*-P-*ethoxyphosphinoylbutanoate* (17) (6·8 g, 74%), m.p. 65–67° (Found: C, 42·8; H, 8·3; P, 13·7. $C_8H_{18}NO_4P$ requires C, 43·2; H, 8·1; P, 13·9). ^{1}H n.m.r. δ ($CDCl_3$) 1·27, t, *J* 7 Hz, $CO_2CH_2CH_3$; 1·32, t, *J* 7 Hz, $POCH_2CH_3$; 1·6–2·3, m, PCH_2CH_2; 2·46, t, *J* 6 Hz, CH_2CO_2; 3·1, s (broad), NH_2. Adding D_2O removes this peak; 4·1, quartet overlapping a quintet, *J* 7 Hz, $POCH_2 + CO_2CH_2$. ν_{max} (Nujol mull) 3310, 3230, 3130, 2920, 1735, 1585, 1455, 1205, 1040, 1010, 970, 940, 800 cm^{-1}. Mass spectrum 223 (M, 1%), 207 (18), 206 (22), 179 (13), 178 (64), 151 (19), 150 (79), 149 (15), 136 (73), 126 (13), 123 (100), 122 (39), 109 (38), 108 (34), 98 (11), 96 (61), 95 (23), 82 (14), 80 (98), 79 (33), 64 (18), 43 (13), 42 (21), 41 (26), 29 (36), 27 (23).

Ethyl 4-(P-*Ethoxy*-P-*methylaminophosphinoyl*)*butanoate* (*18*)

Ethyl 4-(*P*-chloro-*P*-ethoxyphosphinoyl)butanoate (15) (10 g, 0·0413 mol) was added dropwise with shaking to 24% aqueous methylamine (30 ml) at 0°. When the addition was complete the mixture was stirred for an additional hour and allowed to reach room temperature. The mixture was extracted with chloroform (4 × 15 ml). The aqueous layer was evaporated to dryness and the residue dissolved in chloroform. Methylamine hydrochloride was filtered off and the combined extracts dried over anhydrous sodium sulfate. Removal of solvent followed by distillation gave *ethyl 4*-(P-*ethoxy*-P-*methylaminophosphinoyl*)*butanoate* (18) (2 g, 20%), b.p. 85°/0·12 mm (Found: C, 45·2; H, 8·3; P, 13·4. $C_9H_{20}NO_4P$ requires C, 45·6; H, 8·5; P, 13·1). ^{1}H n.m.r. δ (CD_3COCD_3) 1·24, t, *J* 7 Hz, $CO_2CH_2CH_3$; 1·27, t, *J* 7 Hz, $POCH_2CH_3$; 1·5–3·0, m, $CH_2CH_2CH_2PNHCH_3$; 4·1, m, $POCH_2 + CO_2CH_2$. ν_{max} (film) 3230, 2960, 1735, 1660, 1560, 1210, 1040, 950 cm^{-1}.

2-Ethoxy-6-oxo-1,2-azaphosphinane 2-Oxide (*3*)

Ethyl 4-(*P*-amino-*P*-ethoxyphosphinoyl)butanoate (17) (10 g, 0·045 mol) was dissolved in t-butyl alcohol (250 ml) and the mixture dried by azeotropic distillation. The mixture was cooled and potassium t-butoxide (5 g, 0·045 mol) was added in small portions with stirring over 4–5 h. The mixture was refluxed for 1·5 h before the solvent was removed and the residue dissolved in water (30 ml). The mixture was neutralized to pH 7, then thoroughly extracted with dichloromethane (4 × 15 ml). The aqueous layer was evaporated to dryness and extracted with hot benzene (2 × 15 ml). The combined extracts were dried over anhydrous sodium sulfate and evaporated. The solid residue was recrystallized from benzene to give *2-ethoxy-6-oxo-1,2-azaphosphinane 2-oxide* (3) (3·9 g, 50%), m.p. 109–112° (Found: C, 40·8; H, 6·9; P, 17·6. $C_6H_{12}NO_3P$ requires C, 40·7; H, 6·8; P, 17·5). ^{1}H n.m.r. δ ($CDCl_3$) 1·25, t, *J* 7 Hz, CH_3CH_2OP; 1·5–2·5, m, $PCH_2CH_2CH_2$; 4·05, quintet (dq), *J* 7 Hz, $POCH_2$; 7·9, s (broad), NH. ν_{max} (KBr disc) 3100, 1680, 1355, 1295, 1230, 1040, 975,

950, 800 cm^{-1}. Mass spectrum 177 (M, 83%), 150 (73), 149 (22), 134 (16), 133 (42), 132 (36), 121 (23), 107 (44), 106 (100), 105 (19), 93 (10), 90 (17), 80 (25), 78 (57), 65 (60), 64 (10), 57 (28), 55 (16), 47 (23), 42 (78), 41 (60), 39 (30), 29 (20), 27 (28).

2-Ethoxy-1-methyl-6-oxo-1,2-azaphosphinane 2-Oxide (19)

(i) Ethyl 4-(*P*-ethoxy-*P*-methylaminophosphinoyl)butanoate (18) (9·4 g, 0·0396 mol) was dissolved in t-butyl alcohol (250 ml) and the mixture dried by azeotropic distillation. Potassium t-butoxide (4·45 g, 0·0396 mol) was added in small portions over 2·5 h. The mixture was stirred overnight, then refluxed for 1·5 h. The solvent was removed and the residue dissolved in water (30 ml). The mixture was neutralized to pH 7 and thoroughly extracted with dichloromethane (4 × 15 ml). The extracts were dried over anhydrous sodium sulfate, evaporated and distilled to give *2-ethoxy-1-methyl-6-oxo-1,2-azaphosphinane 2-oxide* (19) (0·5 g, 7%), b.p. (bulb to bulb) 80–90°/0·03 mm (Found: P, 15·8. $C_7H_{14}NO_3P$ requires P, 16·2). ^1H n.m.r. δ ($CDCl_3$) 1·36, t, J 7 Hz, CH_3CH_2OP; 1·6–2·7, m, $PCH_2CH_2CH_2$; 2·98, d, J_{PH} 6·5 Hz, NCH_3; 4·18, quintet (d of q), J 7 Hz, $POCH_2$. ν_{max} (film) 2950, 1670, 1290, 1230, 1030, 940 cm^{-1}. Mass spectrum 192 (8%), 191 (M, 100), 164 (15), 163 (26), 162 (14), 147 (59), 146 (21), 135 (32), 134 (19), 119 (17), 107 (35), 106 (76), 105 (12), 94 (17), 93 (10), 90 (13), 81 (10), 80 (13), 78 (42), 70 (69), 70 (17), 68 (26), 65 (51), 58 (10), 56 (14), 55 (38), 47 (28), 43 (13), 42 (71), 41 (59), 39 (27), 30 (28), 29 (28), 26 (28).

(ii) Ethyl 4-(*P*-amino-*P*-ethoxyphosphinoyl)butanoate (17) (10 g, 0·045 mol) was dissolved in t-butyl alcohol (200 ml) and the mixture dried by azeotropic distillation. Potassium t-butoxide (5·5 g, 0·049 mol) was added in small portions with stirring over 4 h. The mixture was stirred overnight before it was refluxed for 30 min. Methyl iodide (7·0 g, 0·049 mol) was added to the mixture and refluxing continued for 4 h. The solvent was evaporated and the residue dissolved in water (30 ml). The mixture was neutralized to pH 7 and thoroughly extracted with chloroform (4 × 15 ml). The extracts were dried over anhydrous sodium sulfate, evaporated and distilled to give 2-ethoxy-1-methyl-6-oxo-1,2-azaphosphinane 2-oxide (19) (5·17 g, 59%), b.p. 104–110°/0·03 mm.

2-Ethoxy-6-oxo-1-(prop-2′-enyl)-1,2-azaphosphinane 2-Oxide (21)

(i) 2-Ethoxy-6-oxo-1,2-azaphosphinane 2-oxide (3) (9·4 g, 0·053 mol) was dissolved in t-butyl alcohol (100 ml) and the mixture dried by azeotropic distillation. Potassium t-butoxide (5·95 g, 0·053 mol) was added in small portions with stirring over 3·5 h at room temperature. Allyl bromide (7·0 g, 0·058 mol) was added and the mixture refluxed for 4 h. The solvent was removed and the residue dissolved in water and neutralized to pH 7. The mixture was extracted with chloroform (3 × 30 ml). The extracts were dried over anhydrous sodium sulfate, evaporated and distilled to give *2-ethoxy-6-oxo-1-(prop-2′-enyl)-1,2-azaphosphinane 2-oxide* (21) (5·8 g, 50%), b.p. 116°/0·02 mm (Found: P, 14·2. $C_9H_{16}NO_3P$ requires P, 14·3). ^1H n.m.r. δ ($CDCl_3$) 1·35, t, J 7 Hz, CH_3CH_2OP; 1·6–2·7, m, $PCH_2CH_2CH_2$; 4·2, m, 4H $NCH_2CH{=}CH_2 + OCH_2$; 5·6–6·3, m, $CH{=}CH_2$. ν_{max} (film) 2960, 1690, 1300, 1275, 1225, 1035, 960 cm^{-1}. Mass spectrum 218 (11%), 217 (M, 100), 202 (18), 189 (58), 174 (25), 173 (13), 163 (16), 162 (32), 160 (57), 146 (17), 145 (20), 136 (22), 134 (19), 13 (34), 132 (23), 122 (11), 107 (10), 106 (19), 105 (18), 102 (12), 97 (47), 96 (13), 93 (16), 92 (10), 82 (39), 80 (16), 78 (14), 70 (15), 69 (36), 68 (16), 65 (32), 57 (14), 56 (44), 55 (25), 54 (18), 47 (22), 43 (12), 42 (32), 41 (90), 39 (37), 32 (12), 30 (12), 29 (25), 26 (33).

(ii) Ethyl 4-(*P*-amino-*P*-ethoxyphosphinoyl)butanoate (17) (10 g, 0·045 mol) was dissolved in t-butyl alcohol (200 ml) and the mixture dried by azeotropic distillation. Potassium t-butoxide (5·5 g, 0·049 mol) was added in small portions with stirring over 3 h. The mixture was stirred overnight before being refluxed for 30 min. Allyl bromide (5·94 g, 0·049 mol) was added and the mixture refluxed for 4 h. The solvent was removed and the residue dissolved in water (40 ml). The mixture was neutralized to pH 7 and extracted with chloroform (4 × 20 ml). The extracts were dried over anhydrous sodium sulfate, evaporated and distilled to give 2-ethoxy-6-oxo-1-(prop-2′-enyl)-1,2-azaphosphinane 2-oxide (21) (5·1 g, 52%), b.p. 126–127°/0·08 mm.

1-Benzyl-2-ethoxy-6-oxo-1,2-azaphosphinane 2-Oxide (11)

Ethyl 4-(*P*-amino-*P*-ethoxyphosphinoyl)butanoate (17) (5 g, 0·0224 mol) was dissolved in t-butyl alcohol (100 ml) and the mixture dried by azeotropic distillation. Potassium t-butoxide (2·75 g, 0·0246 mol) was added in small portions with stirring over 3 h. The mixture was stirred

overnight before being refluxed for 30 min. Benzyl chloride (3·1 g, 0·0246 mol) was added and the mixture refluxed for 15 h. The solvent was removed and the residue dissolved in water (20 ml). The mixture was neutralized to pH 7 and extracted with chloroform (3 × 15 ml). The extracts were dried over anhydrous sodium sulfate, evaporated and distilled (b.p. 125–30°/0·04 mm) to give 2·9 g of a mixture containing approximately 55% of 1-benzyl-2-ethoxy-6-oxo-1,2-azaphosphinane 2-oxide (11), 26% of 6-benzyloxy-2-ethoxy-2,3,4,5-tetrahydro-1,2-azaphosphinine 2-oxide (22) and 19% of 2-ethoxy-6-oxo-1,2-azaphosphinane 2-oxide (3). ^{1}H n.m.r. of the mixture in $CDCl_3$ showed the *N*-benzylic methylene as a multiplet at δ 4·75 while the *O*-benzylic methylene was a singlet at 5·22. ν_{max} (film) 2950, 1685 ($CONCH_2Ph$), 1640 ($N{=}COCH_2Ph$), 1280, 1225, 1030 and 950 cm^{-1}. G.c.–m.s. was used to identify components in the mixture. 1-Benzyl-2-ethoxy-6-oxo-1,2-azaphosphinane 2-oxide (11) had mass spectrum 268 (7%), 267 (M, 37), 239 (32), 210 (25), 161 (11), 152 (14), 147 (32), 146 (21), 136 (86), 132 (15), 108 (49), 106 (20), 105 (13), 104 (37), 93 (14), 92 (19), 91 (100), 80 (50), 79 (11), 78 (18), 77 (29), 65 (42), 51 (19), 47 (15), 42 (18), 41 (42), 39 (29), 29 (38) and 26 (27). 6-Benzyloxy-2-ethoxy-2,3,4,5-tetrahydro-1,2-azaphosphinine 2-oxide (22) had mass spectrum 268 (3%), 267 (M, 18), 161 (63), 133 (20), 93 (34), 91 (100), 65 (29), 41 (23), 39 (12), 29 (14), 26 (11). When benzyl bromide was used as the alkylating agent the reaction yielded 4·0 g of a mixture containing approximately 83% of (11) and 17% of (22). Only trace amounts of (3) were found.

Reaction of Phenyllithium with 2-Ethoxy-6-oxo-1-(prop-2′-enyl)-1,2-azaphosphinane 2-Oxide (21)

2-Ethoxy-6-oxo-1-(prop-2′-enyl)-1,2-azaphosphinane 2-oxide (21) (2 g, 9·2 mmol) was dissolved in ether (40 ml) and cooled to −70° under an atmosphere of nitrogen. Phenyllithium solution (36 ml of 0·26 M, 9·4 mmol) was added dropwise with stirring over 30 min. The mixture was stirred for an additional hour at −70° then allowed to reach room temperature. The mixture was poured into 10% hydrochloric acid (40 ml). Extracting this mixture with ether yielded 0·7 g of a mixture of diphenyl and starting material (21). The aqueous mixture was adjusted to pH 10 and extracted with chloroform to leave an oil (0·25 g). The aqueous layer was neutralized to pH 7 and evaporated to dryness. The residue was extracted with ethanol and the extracts evaporated to leave a high melting (> 300°) solid which contained no phenyl groups. Infrared analysis showed a broad carbonyl stretch at 1645 cm^{-1} which suggested the material was polymeric. G.c.–m.s. analysis of the oil showed one minor and two major products had formed. One of the major products, 4-(*P*-ethoxy-*P*-phenylphosphinoyl)-*N*-(prop-2′-enyl)butanamide (23), was isolated as a solid (*c.* 125 mg, 4·6%) when the oil was distilled, m.p. 98–102°. ^{1}H n.m.r. δ ($CDCl_3$) 1·28, t, *J* 7 Hz, CH_3CH_2OP; 1·6–2·6, m, $PCH_2CH_2CH_2$; 3·06, s, NH. Adding D_2O removed this peak; 4·0, m, $POCH_2+NCH_2$; 5·0–6·5, m, $CH{=}CH_2$; 7·6, m, 5H, ArH. ν_{max} (KBr disc) 3230, 3040, 2900, 1655, 1540, 1438, 1180, 1120, 925, 750, 725, 700 cm^{-1}. Mass spectrum 296 (2%), 295 (M, 15), 240 (15), 239 (100) (M − $NHCH_2CH{=}CH_2$, 100), 212 (18), 211 (239 − CO, 59), 197 (211 − CH_2, 62), 184 ($CH_2{=}P(OH)$-(OEt)Ph, 17), 183 (197 − CH_2, 25), 170 (25), 169 (183 − CH_2, 22), 156 ($PhP(O)(OH)CH_3$, 44), 142 (14), 141 (PhP(O)(OH), 83), 140 ($PhPO_2$, 32), 126 ($CH_2CH_2CH_2CONHCH_2CH{=}CH_2$, 25), 105 (26), 104 (17), 91 (12), 78 (15), 77 (62), (Ph), 56 (23), 51 (13), 47 (12), 41 ($CH_2CH{=}CH_2$, 52). The other major product, 4-(diethoxyphosphinoyl)-*N*-(prop-2′-enyl)butanamide (24) (*c.* 4·7% yield) had mass spectrum 264 (1–2%), 263 (M, 13), 218 (M − OEt, 14), 207 (M − $NHCH_2CH{=}CH_2$, 100), 180 (32), 179 (207 − CO, 42), 165 (179 − CH_2, 55), 152 ($CH_2{=}P(OH)(OEt)_2$, 60), 151 (165 − CH_2, 82), 138 (25), 137 (151 − CH_2, 13), 126 (M − $P(O)(OEt)_2$, 32), 125 (63), 123 ($CH_2{=}P(OH)_2OEt$, 59), 109 (EtOP(O)-OH, 26), 108 ($EtOPO_2$, 21), 105 (14), 99 (11), 97 (25), 84 (12), 81 (20), 80 (11), 65 (13), 57 (21), 56 (43), 42 (18), 41 ($CH_2CH{=}CH_2$, 86), 39 (14), 29 (22) and 26 (15). The minor product was 4-(*P*-ethoxy-*P*-(prop-2′-enoxy)phosphinoyl)-*N*-(prop-2′-enyl)butanamide (25) (*c.* 0·9% yield), mass spectrum 275 (M, 3%), 219 (M − $NHCH_2CH{=}CH_2$, 48), 191 (219 − CO, 17), 179 (10), 177 (191 − CH_2, 17), 151 (28), 136 (20), 124 (10), 123 (20), 107 (10), 106 (11), 81 (15), 57 ($OCH_2CH{=}CH_2$, 14), 56 ($NHCH_2CH{=}CH_2$, 47), 42 (10), 41 ($CH_2CH{=}CH_2$, 100), 39 (15)

Reaction of Phenylmagnesium Bromide with 2-Ethoxy-1-methyl-6-oxo-1,2-azaphosphinane 2-Oxide (19)

2-Ethoxy-1-methyl-6-oxo-1,2-azaphosphinane 2-oxide (19) (2 g, 10·5 mmol) was dissolved in ether and cooled to 0°. Phenylmagnesium bromide solution (22 ml of 0·47 M, 10·5 mmol) was added dropwise with stirring over 20 min. The mixture was stirred at 0° for 30 min before being refluxed for 1 h. The mixture was poured into 10% hydrochloric acid (25 ml) and the pH adjusted to 12.

The mixture was extracted with chloroform. The extracts were dried over anhydrous sodium sulfate and evaporated to give a small amount of oil. The aqueous layer was neutralized to pH 7, evaporated to dryness and extracted with ethanol. The extract was evaporated to leave a solid that contained no phenyl groups. Infrared analysis showed a broad carbonyl stretch at 1650 cm^{-1} which indicated the material may be polymeric. G.c.–m.s. analysis of the oil showed that two products had formed in almost equal proportions. The first was 4-(*P*-ethoxy-*P*-phenylphosphinoyl)-*N*-methylbutanamide (26), mass spectrum 270 (4%), 269 (M, 27), 212 (12), 211 (M − CONHMe, 19), 197 (211 − CH_2, 72), 184 (CH_2=P(OH)(OEt)Ph, 51), 183 (187 − CH_2, 27), 170 (27), 169 (183 − CH_2, 42), 157 (12), 156 (CH_2=P(OH)Ph, 70), 142 (22), 141 (PhP(O)OH, 100), 140 ($PhPO_2$, 56), 125 (14), 105 (33), 104 (35), 100 (M − P(O)(OEt)Ph, 28), 91 (17), 78 (22), 77 (88) (Ph), 58 ($CONHMe_2$, 35), 55 (27), 51 (20), 47 (20), 42 (13), 41 (15), 27 (16). The other compound was 4-(diethoxyphosphinoyl)-*N*-methylbutanamide (27), mass spectrum 238 (3%), 237 (M, 22), 207 (M − NHMe, 12), 192 (M − OEt, 13), 180 (29), 179 (207 − CO, 24), 165 (72), (179 − CH_2, 72), 164 (CH_2=CHP(O)$(OEt)_2$, 15), 152 (CH_2=P(OH)$(OEt)_2$, 100), 151 (165 − CH_2, 42), 138 (25), 137 (151 − CH_2, 23), 125 (97), 123 (EtOP(O)(OH)CH_2, 65), 109 (EtOP(O)OH, 42), 108 ($EtOPO_2$, 30), 105 (15), 100 (M − P(O)$(OEt)_2$, 27), 97 (40), 81 (26), 80 (15), 73 (15), 68 (13), 65 (18), 58 (CONHMe, 47), 55 (18), 43 (12), 42 (23), 41 (34), 31 (14), 30 (11), 29 (12), 27 (28).

Reaction of Potassium t-Butoxide with 2-Ethoxy-6-oxo-1-(prop-2′-enyl)-1,2-azaphosphinane 2-Oxide (21)

2-Ethoxy-6-oxo-1-(prop-2′-enyl)-1,2-azaphosphinane 2-oxide (21) (1·67 g, 7·7 mmol) was dissolved in t-butyl alcohol (20 ml) and the mixture dried by azeotropic distillation. Potassium t-butoxide (0·87 g, 7·7 mmol) was added and an exothermic reaction ensued. The reaction temperature reached 33°. After 40 min, g.l.c. analysis of the reaction mixture showed it to contain approximately 64% of starting material (21), 24% of 4-(diethoxyphosphinoyl)-*N*-(prop-2′-enyl)butanamide (24) and 12% of 4-(*P*-ethoxy-*P*-(prop-2′-enoxy)phosphinoyl)-*N*-(prop-2′-enyl)butanamide (25).

Reaction of Ethyl Iodide and Potassium t-Butoxide with 2-Ethoxy-6-oxo-1-(prop-2′-enyl)-1,2-azaphosphinane 2-Oxide (21)

2-Ethoxy-6-oxo-1-(prop-2′-enyl)-1,2-azaphosphinane 2-oxide (21) (2 g, 9·2 mmol) and ethyl iodide (1·44 g, 9·2 mmol) were dissolved in t-butyl alcohol (40 ml). Potassium t-butoxide (1·03 g, 9·2 mmol) was added in small portions with stirring at room temperature over 2 h. The mixture was refluxed for 4 h. The solvent was removed and the residue dissolved in water (15 ml). The mixture was adjusted to pH 7 and extracted with chloroform (3 × 15 ml). The extracts were dried, over anhydrous sodium sulfate, evaporated and distilled (b.p. 90–5°/0·05 mm) to give an oil (0·98 g). G.c.–m.s. analysis showed the oil to contain approximately 5% of 2-ethoxy-1-ethyl-6-oxo-1,2-azaphosphinane 2-oxide (30). Mass spectrum 206 (5%), 205 (M, 60), 190 (22) (M − CH_3), 178 (10), 177 (M − CH_2=CH_2, 58), 176 (M − CH_2CH_3, 11), 162 (100), 161 (25), 150 (65), 149 (26), 136 (17), 134 (39), 133 (49), 132 (32), 122 (25), 121 (34), 108 (13), 107 (44), 106 (97), 105 (28), 93 (10), 90 (19), 85 (13), 80 (30), 78 (57), 70 (14), 69 (11), 65 (59), 57 (22), 55 (26), 47 (27), 44 (14), 43 (14), 42 (88), 41 (69), 39 (27), 30 (14), 29 (27), 27 (34). The oil contained 12% of 4-(diethoxyphosphinoyl)-*N*-(prop-2′-enyl)butanamide (24) and 5% of its *N*-ethyl derivative 4-(diethoxyphosphinoyl)-*N*-ethyl-*N*-(prop-2′-enyl)butanamide (28). This had the mass spectrum 291 (M, 4%), 207 (M − N(Et)CH_2CH=CH_2, 49), 179 (207 − CO, 19), 154 (M − P(O)$(OEt)_2$, 14), 151 (179 − CH_2CH_2, 45), 123 (27), 85 (12), 84 (N(Et)CH_2CH=CH_2, 100), 41 (32). The oil also contained 54% of 4-(*P*-ethoxy-*P*-(prop-2′-enoxy)-phosphinoyl)-*N*-(prop-2′-enyl)butanamide (25) and 9% of its *N*-ethyl derivative 4-(*P*-ethoxy-*P*-(prop-2′-enoxy)phosphinoyl)-*N*-ethyl-*N*-(prop-2′-enyl)butanamide (29). This had the mass spectrum 303 (M, 3%), 219 (M − N(Et)CH_2CH=CH_2, 41), 191 (219 − CH_2, 23), 151 (21), 123 (14), 85 (11), 84 (N(Et)CH_2CH=CH_2, 100), 81 (17), 42 (12), 41 (CH_2CH=CH_2, 83), 39 (11).

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