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New Routes to Diethyl 1-Alkenylphosphoramidates

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Abstract—New routes to *N*-(diethoxyphosphoryl)imines derived from enolizable carbonyl compounds have been investigated. Three different procedures were studied: (i) the aza-Claisen condensation of ethyl-[*N*-(diethoxyphosphoryl)]-formimidate with enolizable ketones, (ii) the reaction between diethyl *N*-sulfinylphosphoramidate and aliphatic aldehydes, and (iii) the thermally induced reaction of diethyl phosphoramidate with ketone diethyl acetals. With two exceptions in all cases the products were identified as diethyl 1-alkenylphosphoramidates with no spectroscopically detectable amounts of imine tautomers. The aza-Claisen condensation can be recommended as a simple and effective route to diethyl 1-alkenyl-3-oxophosphoramidates.

Introduction

Imines containing α-hydrogens are capable of imine–enamine tautomerism which is similar to keto–enol tautomerism.[1] This type of tautomerism can also be expected for a series of *N*-masked imines, i.e. *N*-sulfonylimines, *N*-diphenylphosphinylimines, and *N*-trimethylsilylimines derived from enolizable carbonyl compounds (Scheme 1).

The literature concerning this problem is, however, scarce and ambiguous. *N*-Sulfonylimines derived from isobutyraldehyde and 3-methylbutanal could not be obtained free from the corresponding tautomeric enamines by the action of *N*-sulfinyl mesitylsulfonamide on the above-mentioned aldehydes in the presence of boron trifluoride etherate.[2] Similarly some *N*-tosylimines prepared from chloramine-T, tellurium metal, and enolizable aldehydes tautomerized completely to the corresponding enamines upon workup.[3] On the other hand Weinreb et al. reported various synthetic applications of *N*-tosylimines prepared 'in situ' from enolizable aldehydes and *N*-sulfinyl-*p*-toluenesulfonamide.[4–7] No difficulties due to *N*-tosylimine tautomerization were encountered in all transformations studied. Some *N*-diphenylphosphinylimines containing α-protons could also be prepared free from the corresponding enamide tautomers by free-radical rearrangement of *O*-phosphonylated oximes.[8–12] In contrast to these observations, however, enolizable *N*-trimethylsilylimines, regardless of the method of their preparation, always existed in tautomeric equilibrium with sizeable amounts of enamines.[13–15]

In connection with our recent interest in possible synthetic applications of *N*-(diethoxyphosphoryl)imines[16,17] we decided to investigate some new potential routes to this class of compounds starting from enolizable carbonyl precursors. The results of these attempts are described herein.

Results and Discussion

Having in mind our earlier unsuccessful attempts in preparing *N*-(diethoxyphosphoryl)imines from diethyl acetals of enolizable aldehydes[18] we turned our attention to the following three synthetic transformations.

1. Aza-Claisen condensation of ethyl-[*N*-(diethoxyphosphoryl)]-formimidate with ketones

Similar to the crossed Claisen condensation between carboxylic esters and ketones, an analogous reaction with phosphorylated iminoester (**1**) could be envisaged. Realization of this conjecture was demonstrated by adding (**1**) at room temperature to the pre-formed enolate prepared from the ketone (**2**) and sodium hydride in tetrahydrofuran. As expected, nucleophilic addition to the carbon–nitrogen double bond took place easily. The azaanion (**3**) formed eliminated ethoxide ion to give *N*-(diethoxyphosphoryl)-imine (**4**). This compound could

Y = SO_2Ar, $P(O)Ph_2$, $SiMe_3$

Scheme 1.

Keywords: imines; enamides; tautomerism.

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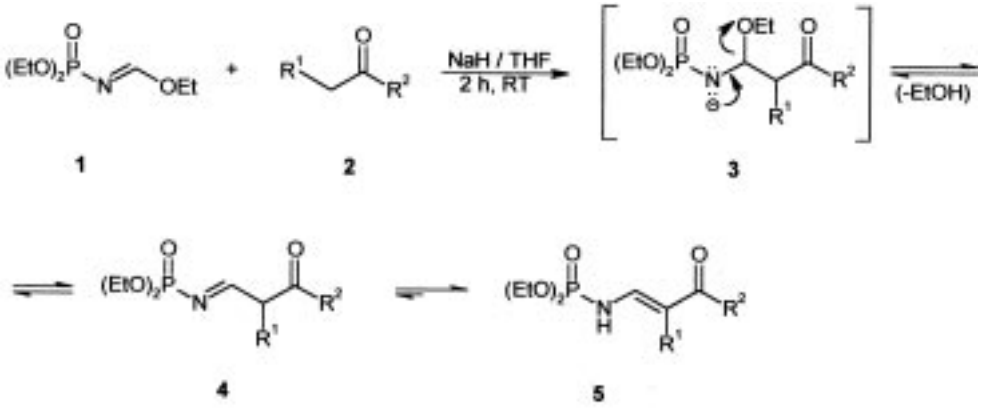


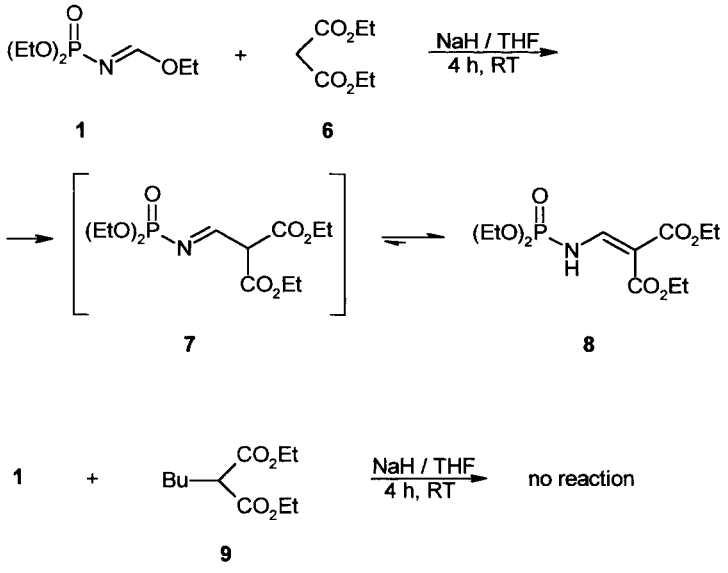
2-5	R^1	R^2	2-5	R^1	R^2
a	H	Me	e	Me	Ph
b	Me	Me	f	$-(CH_2)_5-$	
c	Me	Et	g	$-(CH_2)_4-$	
d	H	Ph			

Scheme 2.

not, however, be isolated because it tautomerized to the thermodynamically more stable, conjugated diethyl 1-alkenyl-3-oxophosphoramidate (**5**) under the reaction conditions. Tautomeric equilibrium was shifted far to the enamide side (Scheme 2).

After acidic workup we were able to isolate only pure enamides (**5**) free from any spectroscopically detectable amounts of the imines (**4**). In our opinion tautomerization of the imine (**4**) into the enamide (**5**) is the driving force of the condensation. It was found that no reaction takes place between the formimidate (**1**) and butyl diethyl malonate (**9**). The *N*-(diethoxyphosphoryl)imine which should be formed in this reaction has no α-proton and therefore cannot tautomerize to the respective enamide. Analogous reaction between (**1**) and diethyl malonate (**6**) occurs easily leading to the enamide (**8**) produced by prototropic shift from the intermediate imine (**7**) (Scheme 3).

All diethyl 1-alkenyl-3-oxophosphoramidates (**5**) prepared by aza-Claisen condensation were characterized by IR and NMR spectroscopy, mass spectrometry and elemental analysis (see Table 1). Crude compounds were not always analytically pure but they could not be purified by distillation or column chromatography due to extensive decomposition. Their structure could be additionally confirmed by reduction with sodium borohydride



Scheme 3.

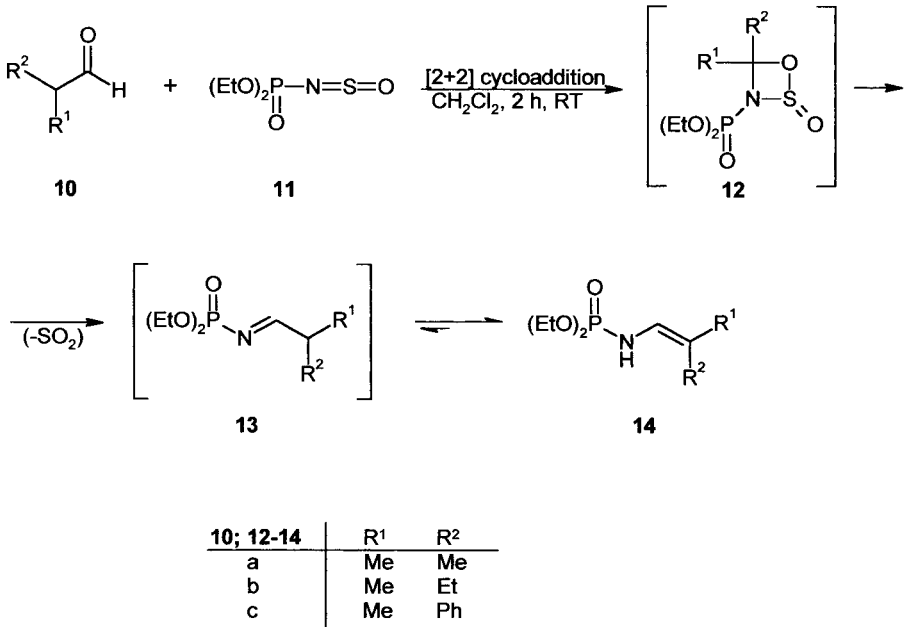
Table 1. Diethyl 1-alkenyl-3-oxophosphoramidates (**5**) and diethyl 1-alkenylphosphoramidates (**14**) and (**17**)

Compound no.	Yield[a] (%)	^{1}H NMR ($CDCl_3$) δ, ppm; *J*, Hz	^{31}P NMR ($CDCl_3$)	IR (film)[b] ν, cm^{-1} δ, ppm	Elemental analyses, *Calc* (Found) %		
					C	H	N
5a	87 (70)	1.348, 1.351 (2t, 6H, *J*=7.0 Hz); 2.16 (s, 3H), 4.04–4.23 (m, 4H); 5.42, 5.44 (dd, 1H, *J*=8.0 Hz, *J*=3.5 Hz); 6.90 (ddd, 1H, *J*=12.5, *J*=9.2 Hz); 10.18 (br t, 1H, *J*=12.5)	1.83	3160, 2984, 2912, 1656, 1596, 1264, 1164, 1040, 968	$C_8H_{16}NO_4P$ (221.19)		
					43.44 (43.20)	*7.29* (7.35)	*6.33* (6.40)
5b	(35)[c]	1.375, 1.378 (2t, 6H, *J*=7.0 Hz); 1.742, 1.894 (2d, 3H, *J*=1.2 Hz); 2.19, 2.26 (2s, 3H) 4.27 (m, 4H); 6.18 (br t, 1H, *J*=12.2); 7.24 (ddq, 1H, *J*=12.2 Hz, *J*=7.5 Hz, *J*=1.2 Hz)	2.34[d] (15%)	3160, 2992, 1636, 1232, 1164, 1104, 1028, 976, 912, 768	$C_9H_{18}NO_4P$ (235.22)		
			2.47 (85%)		*45.96* (46.10)	*7.71* (7.80)	*5.95* (6.20)
5c	82 (40)	1.08, 1.11 (2t, 6H, *J*=7.2 Hz); 1.34, 1.37 (2t, 6H, *J*=7.0 Hz); 1.75, 1.88 (2s, 3H); 2.50, 2.60 (2q, 2H, *J*=7.2 Hz); 4.04–4.32 (m, 4H); 6.04 (br t, *J*=12.0 Hz); 6.76 (dd, *J*=12.0 Hz, *J*=9.3 Hz); 7.25 (dd, *J*=13.2 Hz, *J*=7.5 Hz);10.2 (bt, *J*=13.7 Hz)	2.50[d] (30%)	3168, 2984, 1720, 1636, 1248, 1028, 976, 770	$C_{10}H_{20}NO_4P$ (249.24)		
			2.60 (70%)		*48.19* (48.05)	*8.09* (7.95)	*5.62* (5.80)
5d	87	1.37 (t, 6H, *J*=7.0 Hz); 4.05–4.40 (m, 4H); 6.10–6.40 (m, 1H); 7.15–7.30 (m, 1H); 7.40–7.70 (m, 3H); 7.85–8.10 (m, 2H);10.66 (br t, 1H, *J*=12.5 Hz)	1.72	3160, 2984, 1716, 1636 1586, 1460, 1236, 1032, 968, 828, 756	$C_{13}H_{18}NO_4P$ (283.26)		
					55.12 (54.90)	*6.41* (6.55)	*4.94* (5.05)
5e	86	1.30, 1.31 (2t, 6H, *J*=7.0 Hz); 1.93 (s, 3H); 4.00–4.27 (m, 4H); 6.53 (br t, 1H, *J*=13.5 Hz); 6.94 (ddq, 1H, *J*=13.5 Hz, *J*=7.8 Hz, *J*=1.2 Hz); 7.35–7.60 (m, 5H	2.12	3152, 2984, 1716, 1688, 1628, 1424, 1280, 1248, 1168, 1036, 968, 736	$C_{14}H_{20}NO_4P$ (297.29)		
					56.56 (56.75)	*6.78* (6.80)	*4.71* (4.95)
5f	87	1.35 (t, 6H, *J*=7.0 Hz); 1.80–2.02 (m, 3H); 2.28–2.62 (m, 3H); 4.01–4.27 (m, 4H) 6.43 (br t, 1H, *J*=12.8 Hz), 6.71–6.85, 7.037.19 (2m, 1H)-	2.51[d] (10%)	3136, 2984, 1712, 1628, 1248, 1204, 1164, 1024, 976, 896, 832	$C_{10}H_{18}NO_4P$ (247.23)		
			2.61 (90%)		*48.58* (48.30)	*7.34* (7.20)	*5.67* (5.75)
5g	93	1.30–1.42 (m, 6H); 1.62–1.90 (m, 4H); 2.30–2.43 (m, 4H); 4.01–4.27 (m, 4H); 6.71–6.82 (m, 1H);10.31 (br t, 1H, *J*=13.7 Hz)	2.28[d] (85%)	176, 2984, 2936, 1652, 1584, 1252, 1152, 1028, 976, 920	$C_{11}H_{20}NO_4P$ (261.25)		
			2.51 (15%)		*50.57* (50.30)	*7.72* (7.80)	*5.36* (5.20)
14a	57 (28)	1.34 (t, 6H, *J*=7.1 Hz); 1.55 (br s, 3H); 1.60 (br s, 3H); 4.05–4.13 (m, 4H); 4.58 (br s, 1H); 5.64–5.70 (m, 1H)	5.1	3116, 2984, 2912, 1688, 1244	$C_8H_{18}NO_3P$ (207.21)		
					46.37 (46.17)	*8.76* (9.01)	*6.76* (6.85)
14b	57 (23)	0.98 (t, 3H, *J*=7.5 Hz); 1.34 (t, 6H, *J*=7.1 Hz); 1.55, 1.62 (2br s, 3H); 1.96 (br q, 2H, *J*=7.5 Hz); 4.03–4.25 (m, 4H); 4.53 (br t, 1H, *J*=10.0 Hz); 5.68–5.72 (m, 1H)	5.3	3200, 2976, 1680, 1244	$C_9H_{20}NO_3P$ (221.23)		
					48.86 (48.90)	*9.11* (9.20)	*6.33* (6.50)
14c	80	1.36 (t, 6H, *J*=7.0 Hz); 1.96, 1.97 (2d, 3H, *J*=1.3 Hz); 4.04–4.26 (m, 4H); 4.79 (br t, *J*=12.2 Hz); 5.14 (br t, *J*=11.0 Hz); 6.00 (ddq, *J*=12.2 Hz, *J*=5.8 Hz, *J*=1.3 Hz); 6.34 (ddq, *J*=11.0 Hz, *J*=5.75 Hz, *J*=1.3 Hz); 7.18–7.39 (m, 5H)	4.4[d] (20%)	3200, 2984, 1656, 1240, 1028	$C_{13}H_{20}NO_3P$ (269.28)		
			4.6 (80%)		*57.98* (58.05)	*7.48* (7.60)	*5.20* (5.05)

Table 1 (*continued*)

Compound no.	Yield[a] (%)	^{1}H NMR ($CDCl_3$) δ, ppm; *J*, Hz	^{31}P NMR ($CDCl_3$)	IR (film)[b] ν, cm^{-1} δ, ppm	Elemental analyses, *Calc* (Found) %		
					C	H	N
17a:16a= =15:85	(74)	1.38 (t, 6H, *J*=7.0 Hz); 2.81 (d, 3H, *J*=2.5 Hz); 4.05–4.28 (m, 4H); *4.69 (br s, 1H); 4.86 (s, 1H); 4.96 (br d, 1H, J=10.0 Hz);* 7.36–7.53 (m, 3H); 7.98–8.02 (m, 2H)[e]	2.9 (17a)	1636, 1448, 1248, 1040	$C_{12}H_{18}NO_3P$ (255.25)		
			4.3 (16a)		*56.47* (56.60)	*7.11* (7.30)	*5.49* (5.60)
17b	(16)	1.35 (t, 6H, *J*=7.1 Hz); 1.87–2.38 (m, 6H); 4.05–4.26 (m, 4H); 4.80–4.90 (m, 1H); 5.07 (br d, 1H, *J*=11.0 Hz)	3.3	–	$C_9H_{18}NO_3P$ (219.22)		
					49.31 (49.15)	*8.28* (8.16)	*6.39* (6.20)
17c	(72)	1.10 (t, 6H, *J*=7.0 Hz); 1.31–1.66 (m, 4H); 1.95–2.27 (m, 4H); 3.87–4.13 (m, 4H); 5.40–5.49 (m, 1H); 6.72 (br d, 1H, *J*=9.8 Hz)[f]	3.2	3192, 2984, 2928, 1676, 1464, 1304, 1236, 1208, 1192, 1028	$C_{10}H_{20}NO_3P$ (233.24)		
					51.49 (51.30)	*8.64* (8.70)	*6.01* (6.20)
17d:16d= =90:10[g]	(80)	1.34 (t, 6H, *J*=7.0 Hz); 1.48–2.81 (m, 10 (12)H); 4.02–4.17 (m, 4H); *4.68 (d, 1H, J=6.8 Hz); 5.27 (t, 1H, J=6.8 Hz)*[e]	3.8 (17d)	3200, 2984, 2928, 2848, 1664, 1480, 1444, 1212, 1028	$C_{11}H_{22}NO_3P$ (247.27)		
			2.1 (16d)		53.43 (53.20)	*8.97* (9.10)	*5.66* (5.70)

[a] Yields of crude compounds. Yields of distilled samples are given in brackets.
[b] The strongest absorptions are given.
[c] Crystalline solid obtained by refrigeration of crude product followed by filtration.
[d] Signals of diastereomeric enamides. Approximate amounts of isomers are given in brackets.
[e] Characteristic signals of enamides (**17a**) and (**17d**) are italicized.
[f] Taken in C_6D_6.
[g] The composition of distilled material refrigerated for seven days.



10; 12-14	R^1	R^2
a	Me	Me
b	Me	Et
c	Me	Ph

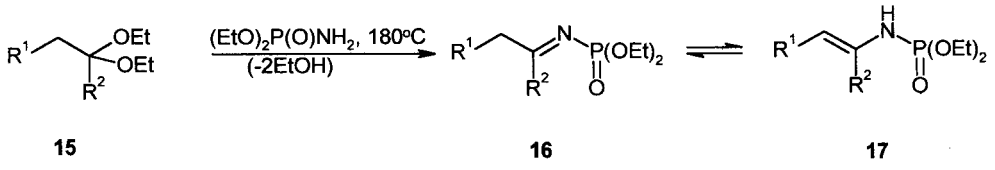
Scheme 4.

in ethanol[19] followed by dephosphorylation with *p*-toluenesulfonic acid in refluxing ethanol.[20] The structure of 3-aminoalkanol tosylates thus formed was proved by elemental analysis and spectroscopic methods (see Experimental).

2. Reactions between diethyl *N*-sulfinylphosphoramidate and aliphatic aldehydes

Following the procedure described by Sisko and Weinreb[7] we attempted to prepare diethyl *N*-(diethoxyphosphoryl)-imines by reacting diethyl *N*-sulfinylphosphoramidate (**11**) with enolizable aldehydes (**10**) in methylene chloride at room temperature. According to the literature suggestions[7,21] the reaction should presumably involve a fleeting [2+2]-cycloadduct (**12**) affording *N*-phosphorylated imine (**13**) on cycloelimination. Surprisingly instead of the expected imine (**13**) the only spectroscopically identified product was the enamide tautomer-diethyl 1-alkenylphosphoramidate (**14**) (Scheme 4).

The absence of detectable amounts of the imine (**13**) was additionally confirmed by the absence of characteristic doublet in the region of 175–185 ppm (J_{CP}=4.4–4.8 Hz) from ^{13}C NMR spectra of all compounds obtained. This doublet is diagnostic for the C=N structural unit linked to P-atom. The reaction was restricted only to branched-chain enolizable aldehydes producing the enamides (**14**) relatively well stabilized by conjugation and/or hyperconjugation. With straight-chain aliphatic aldehydes the reaction did not take place at room temperature but total decomposition was observed at elevated temperature. Yields and spectral data of diethyl 1-alkenylphosphoramidates (**14**) are compiled in Table 1. The reaction is of limited value as a synthetic procedure but in some cases can be a useful alternative to the photoisomerization approach.[22]



15-17	R^1	R^2
a	H	Ph
b	-$(CH_2)_3$-	
c	-$(CH_2)_4$-	
d	-$(CH_2)_5$-	

Scheme 5.

3. Thermal condensation of diethyl phosphoramidate with ketone diethyl acetals

As a result of our preliminary experiments it was found that ketone diethyl acetals (**15**) react with diethyl phosphoramidate slower than aromatic aldehyde diethyl acetals. However, prolonged heating of diethyl phosphoramidate with an excess (2 equiv.) of the corresponding diethyl acetal (**15**) at 160–180°C and removal of the ethanol formed by distillation gave the desired condensation product. Aliphatic ketone diethyl acetals afforded complex mixtures of unidentified compounds. Pure enamides (**17**) or mixtures of imines (**16**) and enamides (**17**), were, however, obtained in reasonable yields from acetophenone diethyl acetal and cycloalkanone diethyl acetals (Scheme 5).

All pure compounds as well as tautomeric mixtures were characterized satisfactorily by elemental analysis and spectral data (see Table 1). The presence of the imine (**16a**,**d**) in equilibrium with the enamide tautomer (**17a**,**d**) was additionally proved by means of a diagnostic doublet at 175–185 ppm (J_{CP}=4.4–4.8 Hz) in ^{13}C NMR spectra of (**16a**,**d**). This signal was absent from the spectra of (**17b**,**c**).

Conclusion

All attempts to obtain *N*-(diethoxyphosphoryl)imines derived from enolizable aldehydes and ketones proved totally unsuccessful. However, at least some of the presented experimental procedures can be used for the preparation of not readily accessible diethyl 1-alkenylphosphoramidates.

Experimental

Solvents were purified in the usual way. Melting points (taken in capillaries) are uncorrected. IR spectra were measured in liquid films using a Specord M 80 (C. Zeiss) instrument. ^1H NMR spectra were recorded on a Bruker AVANCE DPX-250 spectrometer operating at 250 MHz using $CDCl_3$ solutions unless otherwise stated. ^{31}P NMR spectra were recorded at 101.255 MHz with the same spectrometer. Positive chemical shifts are downfield from 85% H_3PO_4. FAB/MS were measured on an APO Electron (Ukraine) Model MI 12001 E mass spectrometer equipped with a FAB ion source (thioglycerol matrix). Xenon was used as ionizing gas. The beam energy was set to 5 keV.

All commercially available starting materials were purchased from Fluka and used without additional purification.

Ethyl-[*N*-(diethoxyphosphoryl)]-formimidate (1). The compound was obtained as described previously.[23] Yield—79%; bp 90–91°C/1 Torr (lit.[23]—bp 88–89°C/0.8 Torr).

Diethyl *N*-sulfinylphosphoramidate (11). The compound was prepared according to the literature procedure[24] from diethyl *N*-(trimethylsilyl)-phosphoramidate[25] and thionyl chloride. Yield—68%; bp 92–94°C/2 Torr; ^{31}P NMR: δ—9.8 ppm (lit.[24]—bp 67°C/0.02 Torr).

Ketone diethyl acetals (15). A mixture of ketone (0.2 mol), triethyl orthoformate (32.6 g, 0.22 mol), anhydrous EtOH (9.2 g, 0.2 mol), and conc. hydrochloric acid (0.2 ml) was left for 3 days at room temperature. An excess of acid was then neutralized with solid K_2CO_3, the mixture was filtered and distilled under reduced pressure.

Acetophenone diethyl acetal (15a). Yield—62%; bp 106–108°C/20 Torr.

Cyclopentanone diethyl acetal (15b). Yield—56%; bp 162–166°C.

Cyclohexanone diethyl acetal (15c). Yield—77%; bp 76–80°C/20 Torr.

Cycloheptanone diethyl acetal (15d). Yield—79%; bp 101–104°C/20 Torr.

Preparation of diethyl 1-alkenyl-3-oxophosphoramidate (5a–g)

General procedure: A solution of ketone (**2**) (0.02 mol) in THF (5 ml) was added dropwise with stirring to the suspension of sodium hydride (0.48 g, 0.02 mol) in THF (10 ml). Stirring was continued at room temperature for 30 min. The mixture was then cooled to 15°C and the solution of ethyl-[*N*-(diethoxyphosphoryl)]-formimidate (**1**) (4.2 g, 0.02 mol) in THF (10 ml) was added dropwise at 15°C. Stirring was continued for 2 h at room temperature, CH_2Cl_2 (50 ml) was then added and the mixture was neutralized with 10% H_2SO_4 aq. The organic phase was separated and the water layer was extracted with CH_2Cl_2 (2×20 ml). Evaporation of the neutralized and dried ($MgSO_4$) organic solution afforded crude diethyl 1-alkenyl-3-oxophosphoramidates (**5a**–**g**). Some of these compounds (**5a**–**c**) could be purified by 'bulb to bulb' distillation under reduced pressure. All products were colorless or pale-yellow oils. The yields and spectroscopic data for the products are listed in Table 1.

Condensation of formimidate (1) with sodium diethyl malonate (6-Na). Diethyl malonate (**6**) (3.2 g, 0.02 mol) was added dropwise with stirring to a suspension of sodium hydride (0.48 g, 0.02 mol) in THF (10 ml). Stirring was continued for 30 min at room temperature and a solution of formimidate (**1**) (4.2 g, 0.02 mol) in THF (5 ml) was added. The mixture was left for 12 h at room temperature. It was then poured into ice-cold water (50 ml), neutralized with 10% H_2SO_4 aq., and extracted with CH_2Cl_2 (50 ml). The organic phase was washed with water, dried ($MgSO_4$) and evaporated under reduced pressure to give 5.65 g (87.5%) of analytically pure compound (**8**) as a colorless oil [Found: C, 44.30; H, 6.90; N, 4.45; P, 9.70. $C_{12}H_{22}NO_7P$ requires C, 44.58; H, 6.86; N, 4.33; P, 9.58%]; ν_{max} (liquid film) 3200, 3000, 1730, 1670, 1602, 1420, 1340, 1230, 1050, 980, 802 cm^{-1}; δ_H 1.30 (6H, t, J=7.2 Hz, CH_3CH_2OCO), 1.35 (3H, t, J=7.2 Hz, $CH_3CH_2OP(O)$),

1.37 (3H, t, J=7.2 Hz, $CH_3CH_2OP(O)$), 4.05–4.27 (4H, m, $CH_3CH_2OP(O)$), 4.29 (4H, q, J=7.2 Hz, CH_3CH_2OCO), 8.12 (1H, dd, J=13.3, 10.5 Hz, =CH), 9.68 (1H, br t, NH); δ_P 0.15.

Reduction of (5a) followed by dephosphorylation. 4-Aminobutan-2-ol tosylate. A solution of (**5a**) (1.1 g, 0.005 mol) in EtOH (5 ml) was added with stirring to the suspension of sodium borohydride (0.76 g, 0.02 mol) in EtOH (15 ml). Stirring was continued for 12 h at room temperature. Solvent was then evaporated and the residue was dissolved in $CHCl_3$ (50 ml). The solution was washed with water (2×15 ml), dried ($MgSO_4$) and evaporated. The solution of *p*-toluenesulfonic acid monohydrate (0.95 g, 0.005 mol) in EtOH (10 ml) was added to the residue and the mixture was refluxed for 6 h. It was then concentrated, diluted with Et_2O (30 ml) and refrigerated overnight. Crystalline tosylate was filtered off and recrystallized from EtOH–Et_2O. Colorless leaflets, yield 0.85 g (65%), mp 78–80°C; [Found: C, 50.42; H, 7.50; N, 5.45. $C_{11}H_{19}NO_4S$ requires C, 50.55; H, 7.33; N, 5.36%]; ν_{max} (KBr) 3480, 3200, 2900, 1604, 1510, 1200, 1140, 1100, 1050, 800, 775, 700 cm^{-1}; δ_H (D_2O) 1.20, (3H, d, J=6.3 Hz, CH_3CH), 1.66–1.90 (2H, m, $CH_2CH_2NH_3^+$), 2.38 (3H, s, $CH_3C_6H_4$), 3.08 (2H, t, J=7.5 Hz, CH_2CH_2 NH_3^+), 3.94 (1H, sextet, J=6.3 Hz, CH_3CH), 7.36–7.72 (4H, AA′ XX′ system, C_6H_4); FAB/MS 262 (M+1).

Reduction of (5d) followed by dephosphorylation. 3-Amino-1-phenylpropan-1-ol-tosylate. The transformation of (**5d**) into 3-amino-1-phenylpropan-1-ol tosylate was carried out as described immediately above starting from 0.005 mol of (**5d**). Yield — 0.92 g (57%) of a white solid, mp 174–177°C; [Found: C, 59.30; H, 6.70; N, 4.51. $C_{16}H_{21}NO_4S$ requires C, 59.42; H, 6.54; N, 4.33%]; ν_{max} (KBr) 3300, 3080, 3000, 2880, 1670, 1510, 1460, 1230, 1180, 1140, 930, 800, 770, 700 cm^{-1}; δ_H (DMSO-d_6) 1.76–1.88 (2H, m, $CHCH_2$), 2.28 (3H, s, $CH_3C_6H_4$), 2.80–2.91 (2H, m, $CH_2NH_3^+$), 4.67 (1H, t, J=7.0 Hz, CH), 7.33 (5H, s, C_6H_5), 7.07–7.52 (4H, AA′XX′ system, C_6H_4): FAB/MS: 324 (M+1).

Preparation of diethyl 1-alkenylphosphoramidates (14)

General procedure: A mixture of diethyl *N*-sulfinylphosphoramidate (**11**) (3.98 g, 0.02 mol), aliphatic aldehyde (**10**) (0.02 mol) and CH_2Cl_2 (30 ml) was stirred under nitrogen at room temperature. for 2 h. The solvent was then removed under reduced pressure and the residue was purified by 'bulb to bulb' distillation in vacuo. Compound (**14c**) could not be distilled without decomposition. Distilled enamides (**14a**,**b**) were contaminated with small amounts of unidentified impurities but could be satisfactorily analyzed. Enamides (**14a–c**) are unstable liquids decomposing slowly even on refrigeration.

Thermal condensation of ketone diethyl acetals (15) with diethyl phosphoramidate

General procedure: A mixture of diethyl phosphoramidate (6.12 g, 0.04 mol) and ketone diethyl acetal (**15**) (0.08 mol) was placed in a distillation flask and heated up to 180°C in the reacting mixture until EtOH distilled off. The residue was distilled in vacuo to give the forerun consisting of the acetal (**15**) used in excess. The high boiling fraction was pure enamide (**17**) or a tautomeric mixture of (**17**) and (**16**). Both compounds were colorless liquids.

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