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# A Simple and Efficient Strategy for the Preparation of 5-Phosphorylated Imidazol-2-ones from Primary β-Enaminophosphonates.

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*Abstract-* An easy and efficient synthesis of imidazol-2-ones **5** substituted with a phosphonate group in the 5-position is described. The key step is a heterocyclization of functionalized enamines **3**.These compounds **3** are formed by addition of primary β-enaminophosphonates **1** to diethyl azodicarboxylate **2**. 

Imidazol-2-one ring systems represent an important class of compounds.[1] They may be formed by the reaction of angiotensin I with ascorbate under physiological conditions[2a] and may be useful as antioxidants in vivo.[2b] Likewise, imidazol-2-ones constitute a part of the backbone of the nucleoside antibiotic Nikkomycin X isolated from *Streptomyces tendae*,[3] and imidazol-2-ones have shown anticonvulsant activity[4a] and have been used as selective prostaglandin D2 receptor agonists for the study of intraocular pressure regulation[4b] and as cardiotonic vasodilators[4c] such as enoximone[4d] and piroximone.[4e] In this context, we are interested in the design of new imidazol-2-one derivatives substituted with a phosphonate group in the 5 position of the heterocyclic system. This substitutent could regulate important biological functions and could increase the biological activity of these types of compounds, in a similar way to that reported for other pharmaceuticals.[5] Classical approaches[1] to imidazol-2-ones involving acyclic[6a] and heterocyclic precursors[6b] have been reported. However, to the best of our knowledge, the synthesis of phosphorus substituted imidazol-2-ones has not been reported.


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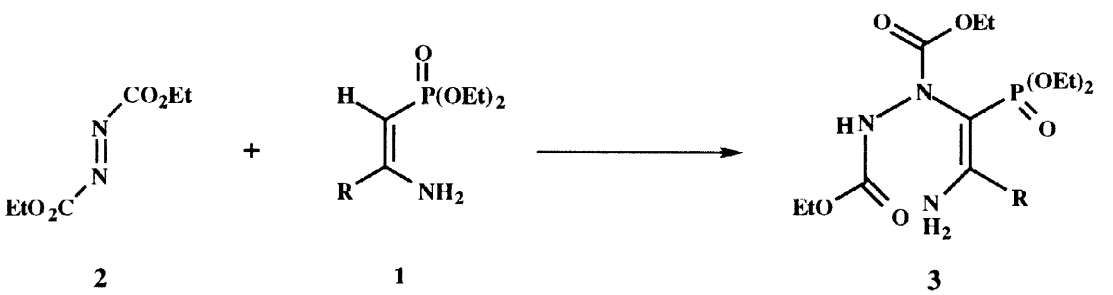
In connection with our interest in the synthesis of five[7] and six[8] membered phosphorylated nitrogen heterocycles we have used β-functionalized enamines derived from phosphazenes, phosphonium salts, phosphine oxides and phosphonates as synthetic intermediates in the synthesis of acyclic derivatives such as oximes,[9a] allylamines,[9b] hydrazones,[9c] and β-amino functionalizaed compounds[9d,e] as well as of phosphorus containing heterocycles.[10] Furthermore, in previous papers we have reported a preparation of primary β-enamines derived from phosphazenes[11] and from phosphonates[8b] and we have used them in the synthesis of cyclic[8b,10,12] and acyclic[9c,11] compounds. Continuing with our interest in the synthesis of new phosphorus substituted heterocycles and with the reactivity of functionalized enamines, we report here an easy and high yielding synthesis of 5-phosphonylimidazol-2-ones **5** from primary β -enaminophosphonates **1** and diethyl azodicarboxylates **2**.

Primary enamines exhibit marked ambident nucleophilicity,[11] but when primary β-enamino-phosphonates **1** were allowed to react with an equimolecular amount of diethyl azodicarboxylate **2** in refluxing THF, functionalized enamines **3** were obtained (see table 1) in a regioselective fashion (Scheme 1). The structure of the 1:1 adducts **3** is supported by the spectroscopic data. Mass spectrometry of **3a** showed the molecular ion peak (m/z, 430, 25%) and in the $^{13}$C-nmr spectrum of compound **3a**, the absence of coupling constant observed in the *ipso* aromatic carbon ($^{3}J_{PC}$ =0 Hz) can be taken as a steady indication for the inversion of the Z-configuration[8b,9e] around the enaminic moiety (C2-C3) of functionalized primary β-enaminophosphonates **3** related to the starting enamine **1**. In $^{31}$P-nmr there appeared two values for the adducts **3** separated by δ=0.5 ppm aproximately, which suggests the existence of two conformers in solution for these compounds. Formation of these compounds **3** can be explained through regioselective addition of enamine **1** to diazene linkage of azodicarboxylate in a similar way to that previously reported for tertiary enamines[13] (Scheme 1).

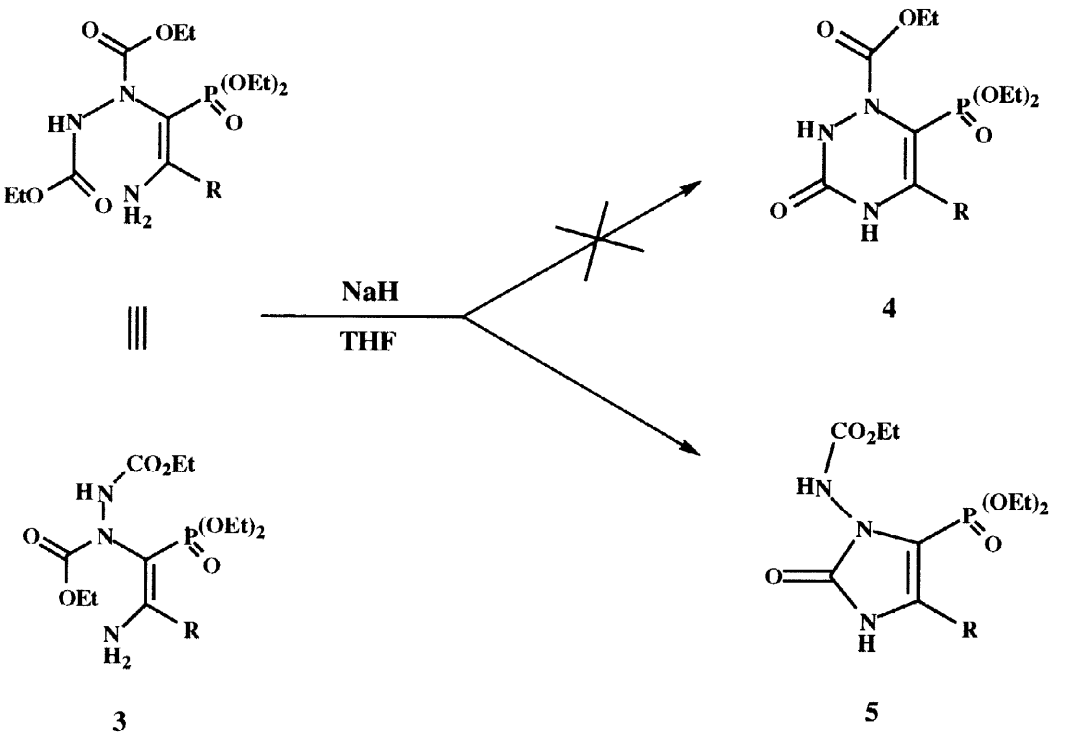



2 1 3

Scheme 1

Compounds **3** were thermally stable and did not cyclize in refluxing toluene for 72 hours. However, enamines **3** underwent cyclocondensation to an heterocyclic compound **4** or **5** by expulsion of a molecule of ethanol when adducts **3** were treated with sodium hydride in tetrahydrofuran (Scheme 2) and can alternatively be prepared in "one pot" synthesis from β-enamines **1**, when crude 1:1 adducts **3** are directly treated, without their isolation, with sodium hydride in THF. Mass spectrometry of heterocyclic compounds **4a** or **5a** showed the molecular ion peak (m/z, 384, 100%) and the cyclocondensation seems

to involve the enamine moiety and either of the two ethoxycarbonyl groups bonded to the nitrogen atoms, while the $^{13}$C-nmr spectrum of this compound **4a** or **5a** showed absorption at $\delta_C$=151.8 ppm with a $^3J_{PC}$=9.8 Hz assignable to the urea carbonyl group, as well as doublets at $\delta_C$=130.6 ppm with a $^2J_{PC}$=20.1 Hz and $\delta_C$=110.0 ppm with a $^1J_{PC}$=229.1 Hz for the heterocyclic carbon atoms. On the other hand, the presence of an intermolecular and an intramolecular hydrogen bond is supported by two peaks 3157 cm$^{-1}$ and 3401 cm$^{-1}$ in the FT-IR spectrum of a highly dilute (0.0625M) $CH_2Cl_2$ solution of **4a** or **5a** and this result could be consistent not only with **4a** but also with **5a**. Therefore, microanalytical, mass-, and spectroscopic data could be in agreement with both of these structures **4** or **5**. In order to confirm and establish if the product, obtained in the cyclocondensation of compounds **3** with a base, corresponds to a five or to a six membered heterocycle, X-ray analysis of the crystalline compound **5a** was performed.




Scheme 2

The structure of imidazol-2-one **5a** was determined by X-Ray analysis (Fig. 1). There are several hydrogen bonds present in the structure; among them, there is an intramolecular bond linking the oxygen atom of the 2-imidazolone ring with the exocyclic NH group. In addition, it is worth noting the presence of a intermolecular hydrogen bond between the oxygen of the phosphonate and the NH group of the 2-imidazolone ring, which could be responsible for the relative orientation of the phosphonate. On the other hand, the 2-pyridine ring is rotated 28° from the 2-imidazolone ring. Finally, the presence of unusually high thermal factors for the terminal carbon in one of the ethoxy groups of the phosphonate, led us to a disordered model for that part of the molecule.

**Table 1.** Functionalized enamines **3** and imidazol-2-ones **5**.

| Compound | R | | Yield (%) | mp (°C) |
|---|---|---|---|---|
| **3a** | 2-pyridyl | | 84[b] | 110-112 |
| **3b** | phenyl | | 91[b] | 126-127 |
| **3c** | *p*-tolyl | | 87[b] | 145-146 |
| **3d** | 2-thiophenyl | | 85[b] | 113-115 |
| **3e** | 2-furyl | | 88[b] | 101-102 |
| **5a** | 2-pyridyl | 91[a] | 93[b] | 158-159 |
| **5b** | phenyl | 94[a] | 96[b] | 180-182 |
| **5c** | *p*-tolyl | | 95[b] | 184-185 |
| **5d** | 2-thiophenyl | | 90[b] | 168-170 |
| **5e** | 2-furyl | 93[a] | 93[b] | 170-171 |

[a]Yield of isolated products **5** based on **1** in a "one pot" reaction. [b]Yield of isolated products based on **3**.

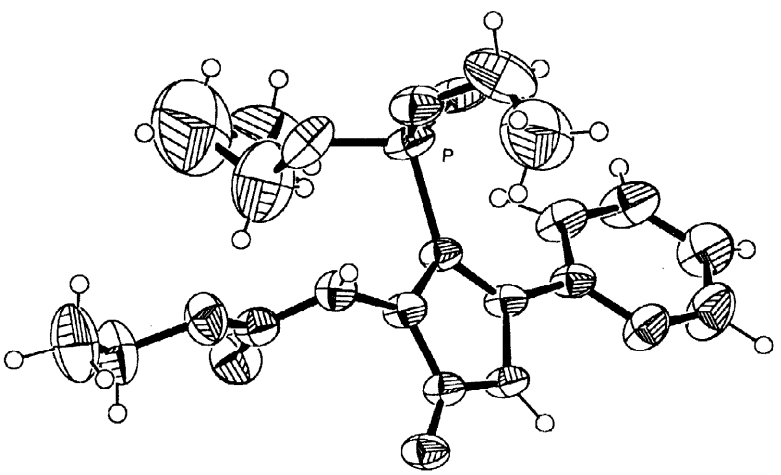



Figure 1 . *ORTEP* drawing of the X-ray crystale structure of imidazol-2-one **5a**.

In conclusion, to the best of our knowledge, this route describes the first synthesis of phosphorylated imidazol-2-ones **5** making use of readily available starting materials. Imidazol-2-ones **5** may be key intermediates for the preparation of biologically active compounds such as nucleoside antibiotics[3a] and are useful compounds in medicinal chemistry since these products display a broad range of biological activities and have been widely used as pharmaceuticals.[2-5]

## ACKNOWLEDGEMENTS

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## EXPERIMENTAL SECTION

General. Melting points were determined with a Buchi SPM-20 apparatus and are uncorrected. Analytical *TLC* was performed on 0.25mm silica gel plates (Merck). Visualization was accomplished by *UV* light and iodine. Solvents for extraction were technical grade and distilled from the indicated drying agents: *THF* (sodium benzophenone ketyl); toluene (*Na*). All solvents used in reactions were freshly distilled from appropriate drying agents before use: *THF* (sodium benzophenone ketyl), toluene (*Na*). All other reagents were recrystallized or distilled as necessary. Mass spectra were obtained on a Hewlett Packard 5890 spectrometer. Infrared spectra were taken on a Nicolet IRFT Magna 550 spectrometer. *$^1$H-NMR* spectra were recorded on a Varian 300 MHz spectrometer using tetramethylsilane (0.00 ppm) or chloroform (7.26 ppm) as an internal reference in *$CDCl_3$* solutions. *$^{13}$C-NMR* spectra were recorded at 75 MHz with chloroform (77.0 ppm) as an internal reference in *$CDCl_3$* solutions. *$^{31}$P-NMR* spectra were recorded at 120 MHz with 85% phosphoric acid as an external reference. Elemental analyses were performed in a Leco CHNS-932 instrument. Chemical shifts are given in ppm *($\delta$)*; multiplicities are indicated by s (singlet), d (doublet), dd (double-doublet), t (triplet) q (quadruplet) or m (multiplet). Coupling constants, *J*, are reported in hertz. Infrared spectra *(IR)* were obtained as solids in *KBr*. Peaks are reported in $cm^{-1}$. Mass spectra *(EI)* were obtained with a ionization voltage of 70 eV. Data are reported in the form m/z (intensity relative to base = 100). All reactions were performed in oven (125 °C) or flame-dried glassware under an inert atmosphere of dry $N_2$.

**General Procedure for the Preparation of the functionalizated β-enaminophosphonates 3.** A dry flask, 100-ml, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with 1..27 g (5 mmol) of β-enaminophosphonate **1** (R=phenyl), and 25 mL of THF. A solution 0.8 ml (5 mmol) of diethyl azadicarboxylate **2** and 10 mL of THF was added over 10 min. The mixture was stirred and refluxed until *TLC* indicated the disappearance of the β-enaminophosphonate **1** (1 day). The mixture was concentrated and the crude product was purified by recrystallization (AcOEt).

**3-Ethoxycarbonil 2-(2-amine 1-diethoxyphosphoryl 2-(2-pyridyl) ethenyl) carbazate (3a)**. 1827 mg (84 %) of **3a** as a white solid. Data for **3a**: mp 110-112 °C; $^{1}H$-*NMR* (300 MHz): 0.91 (s, 3H, $CH_3$), 1.18 (s, 3H, $CH_3$), 1.25 (t, 8H, $^{3}J_{HH}$= 6.9 Hz, $CH_3$ and $NH_2$), 3.59 (s, 2H, $OCH_2$), 3.92 (s, 2H, $OCH_2$), 4.18 (q, 5H, $^{3}J_{HH}$= 6.9 Hz, $OCH_2$ and NH), 7.28-8.58 (m, 4H, arom). $^{13}C$-*NMR* (75 MHz): 14.1 ($CH_3$), 15.5 ($CH_3$), 15.9 ($CH_3$), 60.9 ($OCH_2$), 61.9 ($OCH_2$), 62.8 ($OCH_2$), 96.7 (d, $^{1}J_{PC}$= 243.7 Hz, =C-P), 124.4-148.8 (CH-arom), 152.3 (C-*ipso,arom.*), 155.6-158.2 (C-N, C=O, C=O). $^{31}P$-*NMR* (120 MHz). 19.5 and 20.1; *IR* (*KBr*) 3480, 3306, 3227, 3157, 1737, 1702, 1260 $cm^{-1}$; *MS* (EI) 430 ($M^+$, 25). Anal. Calcd for $C_{17}H_{27}N_4O_7P$: C, 47.44; H, 6.37; N, 13.00. Found: C, 46.66; H, 6.36; N, 12.52.

**3-Ethoxycarbonil 2-(2-amine 1-diethoxyphosphoryl 2-phenyl ethenyl) carbazate (3b)**. 1951 mg (91 %) of **3b** as a white solid. Data for **3b**: mp 126-127 °C; $^{1}H$-*NMR* (300 MHz): 0.92 (s, 3H, $CH_3$), 1.12 (s, 3H, $CH_3$), 1.25 (t, 8H, $^{3}J_{HH}$= 7.2 Hz, $CH_3$ and $NH_2$), 3.61 (s, 2H, $OCH_2$), 3.83 (s, 2H, $OCH_2$), 4.17 (q, 5H, $^{3}J_{HH}$= 7.2 Hz, $OCH_2$ and NH), 7.31-7.46 (m, 5H, arom). $^{13}C$-*NMR* (75 MHz): 14.2 ($CH_3$), 15.6 ($CH_3$), 16.1 ($CH_3$), 60.8 ($OCH_2$), 62.2 ($OCH_2$), 62.7 ($OCH_2$), 96.8 (d, $^{1}J_{PC}$= 245.2 Hz, =C-P), 126.7-129.7 (CH-arom), 134.9 (C-*ipso,arom.*), 158.2-160.8 (C-N, C=O, C=O). $^{31}P$-*NMR* (120 MHz). 19.5 and 20.1; *IR* (*KBr*) 3378, 3309, 3255, 3209, 1743, 1712, 1212 $cm^{-1}$; *MS* (EI) 429 ($M^+$, 25). Anal. Calcd for $C_{18}H_{28}N_3O_7P$: C, 50.34; H, 6.52; N, 9.79. Found: C, 50.75; H, 6.51; N, 9.77.

**3-Ethoxycarbonil 2-(2-amine 1-diethoxyphosphoryl 2-(*p*-tolyl) ethenyl) carbazate (3c)**. 1927 mg (87 %) of **3c** as a white solid. Data for **3c**: mp 145-146 °C; $^{1}H$-*NMR* (300 MHz): 0.93 (s, 3H, $CH_3$), 1.12 (s, 4H, $CH_3$ and NH), 1.21 (t, 6H, $^{3}J_{HH}$= 7.0 Hz, $CH_3$), 2.31 (s, 3H, $CH_3$), 3.66 (s, 2H, $OCH_2$), 3.87 (s, 2H, $NH_2$), 4.16 (q, 6H, $^{3}J_{HH}$= 7.0 Hz, $OCH_2$), 7.10-7.35 (m, 4H, arom). $^{13}C$-*NMR* (75 MHz): 14.7 ($CH_3$), 16.0 ($CH_3$), 16.4 ($CH_3$), 21.6 ($CH_3$), 61.1 ($OCH_2$), 62.3 ($OCH_2$), 63.2 ($OCH_2$), 97.2 (d, $^{1}J_{PC}$= 212.6 Hz, =C-P), 128.5-128.8 (CH-arom), 132.3 (C-*ipso,arom.*), 140.1 (C-*ipso,arom.*), 156.3-160.8 (C-N, C=O, C=O). $^{31}P$-*NMR* (120 MHz). 19.5 and 20.1; *IR* (*KBr*) 3414, 3304, 3226, 3144, 1740, 1712, 1249 $cm^{-1}$; *MS* (EI) 443 ($M^+$, 6). Anal. Calcd for $C_{18}H_{28}N_3O_7P$: C, 51.47; H, 6.78; N, 9.48. Found: C, 51.66; H, 6.86; N, 9.43.

**3-Ethoxycarbonil 2-(2-amine 1-diethoxyphosphoryl 2-(2-thiophenyl) ethenyl) carbazate (3d)**. 1849 mg (85 %) of **3d** as a white solid. Data for **3d**: mp 113-115 °C; $^{1}H$-*NMR* (300 MHz): 1.07 (s, 3H, $CH_3$), 1.30 (s, 3H, $CH_3$), 1.34 (t, 6H, $^{3}J_{HH}$= 7.2 Hz, $CH_3$), 3.79 (s, 2H, $OCH_2$), 4.02 (s, 2H, $OCH_2$), 4.26 (q, 5H, $^{3}J_{HH}$= 7.2 Hz, $OCH_2$ and NH), 5.82 (s, 2H, $NH_2$), 7.08-7.59 (m, 3H, arom). $^{13}C$-*NMR* (75 MHz): 14.6 ($CH_3$), 16.0 ($CH_3$), 16.4 ($CH_3$), 61.5 ($OCH_2$), 62.5 ($OCH_2$), 63.3 ($OCH_2$), 98.2 (d, $^{1}J_{PC}$= 242.6 Hz, =C-P), 127.4-130.6 (CH-arom), 134.9 (C-*ipso,arom.*), 156.6-158.6 (C-N, C=O, C=O). $^{31}P$-*NMR* (120 MHz). 19.6 and 20.1; *IR* (*KBr*) 3447, 3302, 3216, 3177, 1741, 1710, 1248 $cm^{-1}$; *MS* (EI) 435 ($M^+$, 40). Anal. Calcd for $C_{16}H_{26}N_3O_7PS$: C, 44.13; H, 5.97; N, 9.65; S, 7.35. Found: C, 44.24; H, 6.06; N, 9.69; S, 7.28.

**3-Ethoxycarbonil 2-(2-amine 1-diethoxyphosphoryl 2-(2-furyl) ethenyl) carbazate (3e)** 1844 mg (88 %) of **3e** as a brown solid. Data for **3e**: mp 101-102 °C; $^{1}H$-*NMR* (300 MHz): 1.06 (s, 3H, $CH_3$), 1.23 (m, 9H, $CH_3$), 2.68 (s, 1H, NH), 4.15 (m, 8H, $OCH_2$), 6.05 (s, 2H, $NH_2$), 6.42-7.44 (m, 3H, arom). $^{13}C$-*NMR* (75 MHz): 14.3 ($CH_3$), 15.9 ($CH_3$), 16.1 ($CH_3$), 61.3 ($OCH_2$), 62.2 ($OCH_2$), 63.1 ($OCH_2$), 95.6 (d, $^{1}J_{PC}$= 239.7 Hz, =C-P), 111.8-143.5 (CH-arom), 145.6 (C-*ipso,arom.*), 148.6-158.5 (C-N, C=O, C=O). $^{31}P$-*NMR* (120 MHz). 19.5 and 20.0; *IR* (*KBr*) 3407, 3301, 3217, 3146, 1742, 1711, 1268 $cm^{-1}$; *MS* (EI) 419 ($M^+$, 36). Anal. Calcd for $C_{16}H_{26}N_3O_8P$: C, 45.82; H, 6.20; N, 10.00. Found: C, 44.97; H, 6.18; N, 9.68.

**General Procedure for the Preparation of the Imidazol-2-ones 5.** A dry flask, 100-ml, 2-necked, fitted with a dropping funnel, gas inlet, and magnetic stirrer, was charged with 0.15 g (6.25 mmol) of sodium hydride and 25 mL of THF, this solution is cooled at 0°C, and then a solution (5 mmol) of functionalizated enamine (**3**) and 10 mL of THF was added over 10 min. The mixture was stirred until *TLC* indicated the disappearance of functionalizated enamine (**3**) (1 day). The mixture was concentrated and the crude product was purified by recrystallization (AcOEt).

**1-Amine Carboxylate 4-(2-pyridyl) 5-diethoxyphosphoryl imidazol-2-ones (5a).** 1785 mg (93 %) of **5a** as a white solid. Data for **5a**: mp 158-159 °C; $^{1}H$-*NMR* (300 MHz) 1.28 (m, 9H, $CH_3$), 4.17 (m, 6H, $OCH_2$), 7.22-8.51 (m, 4H, arom), 7.91 (s, 1H, NH), 9.70 (s, 1H, NH); $^{13}C$-*NMR* (75 MHz) 15.8 ($CH_3$), 16.1 ($CH_3$), 62.4 ($OCH_2$), 63.0 ($OCH_2$), 110.0 (d, $^{1}J_{PC}$= 229.1 Hz, =C-P), 123.8-148.7 (C-arom), 130.6 (d, $^{2}J_{PC}$= 20.1 Hz, =C-N), 151.8 (d, $^{3}J_{PC}$= 9.8 Hz, C=O), 155.4 (O-

C=O); *$^{31}$P-NMR* (120 MHz) 4.3; *IR (KBr)* 3393, 3165, 1756, 1708, 1242, cm$^{-1}$; *MS* (EI) 384 (M$^+$, 100). Anal. Calcd for $C_{15}H_{21}N_4O_6P$: C, 46.87; H, 5.47; N, 14.58. Found: C, 46.79; H, 5.41; N, 14.67.

**X-Ray Analysis of imidazol-2-one (5a).** A yellowish prismatic crystal of $C_{15}H_{21}O_6N_4P$ having approximate dimensions of 0.30 X 0.30 X 0.30 mm was mounted on a glass fiber. All measurements were carried out by means of a Enraf-Nonius CAD4 diffractometer with graphite monochromated MoK$\alpha$ radiation. Crystal data: $C_{15}H_{21}O_6N_4P$, T = 293 K, monoclinic, space group P2$_1$/n, with a = 8.778(2) Å, b = 12.158(2) Å, c = 17.742(4) Å, $\gamma$ = 95.75(1) °, V = 1883.8(7) Å$^3$ and Z = 4 ($d_{calc}$ = 1.355 g cm$^{-3}$), m (MoK$\alpha$) = 0.18 mm$^{-1}$, no absorption correction; 3316 unique reflections and all of them were used in refinement; R = 6.6%, $R_w$ = 16.0% for all reflections (R = 4.4% for reflections with $F_o > 4\sigma(F_o)$). The crystal data have been deposited at the Cambridge Crystallographic Data Centre.

**1-Amine Carboxylate 4-phenyl 5-diethoxyphosphoryl imidazol-2-ones (5b).** 1838 mg (96 %) of **5b** as a white solid. Data for **5b**: mp 180-182 °C; *$^1$H-NMR* (300 MHz) 0.92 (s, 3H, $CH_3$), 1.20 (s, 6H, $CH_3$), 4.04 (s, 2H, $OCH_2$), 4.14 (s, 4H, $OCH_2$), 7.22-7.46 (m, 5H, arom), 8.36 (s, 1H, NH), 11.17 (s, 1H, NH); *$^{13}$C-NMR* (75 MHz) 14.7 ($CH_3$), 16.4 ($CH_3$), 62.6 ($OCH_2$), 63.1 ($OCH_2$), 108.1 (d, $^1J_{PC}$= 235.1 Hz, =C-P), 128.3-130.2 (C-arom), 133.1 (d, $^2J_{PC}$= 19.1 Hz, =C-N), 153.8 (d, $^3J_{PC}$= 10.5 Hz, C=O), 155.9 (O-C=O); *$^{31}$P-NMR* (120 MHz) 4.8; *IR (KBr)* 3396, 3171, 1761, 1705, 1246, cm$^{-1}$; *MS* (EI) 383 (M$^+$, 68). Anal. Calcd for $C_{16}H_{22}N_3O_6P$: C, 50.13; H, 5.74; N, 10.96. Found: C, 50.32; H, 5.82; N, 10.92.

**1-Amine Carboxylate 4-(*p*-tolyl) 5-diethoxyphosphoryl imidazol-2-ones (5c).** 1885 mg (95 %) of **5c** as a white solid. Data for **5c**: mp 184-185 °C; *$^1$H-NMR* (300 MHz) 0.98 (t, 3H, $^3J_{HH}$= 6.9 Hz, $CH_3$), 1.22 (t, 6H, $^3J_{HH}$= 6.9 Hz, $CH_3$), 2.28(s, 3H, $CH_3$), 4.04 (q, 2H, $^3J_{HH}$= 6.9 Hz, $OCH_2$), 4.16 (q, 4H, $^3J_{HH}$= 6.9 Hz, $OCH_2$), 7.09-7.39 (m, 4H, arom), 7.78 (s, 1H, NH), 10.74 (s, 1H, NH); *$^{13}$C-NMR* (75 MHz) 14.6 ($CH_3$), 16.2 ($CH_3$), 62.4 ($OCH_2$), 62.8 ($OCH_2$), 107.4 (d, $^1J_{PC}$= 236.7 Hz, =C-P), 125.2-139.8 (C-arom), 133.2 (d, $^2J_{PC}$= 19.1 Hz, =C-N), 153.6 (d, $^3J_{PC}$= 9.6 Hz, C=O), 155.7 (O-C=O); *$^{31}$P-NMR* (120 MHz) 5.5; *IR (KBr)* 3391, 3148, 1754, 1712, 1236, cm$^{-1}$; *MS* (EI) 397 (M$^+$, 100). Anal. Calcd for $C_{17}H_{24}N_3O_6P$: C, 51.38; H, 6.04; N, 10.58. Found: C, 51.03; H, 5.96; N, 10.44.

**1-Amine Carboxylate 4-(2-thiophenyl) 5-diethoxyphosphoryl imidazol-2-ones (5d).** 1750 mg (90 %) of **5d** as a white solid. Data for **5d**: mp 168-170 °C; *$^1$H-NMR* (300 MHz) 1.17 (m, 9H, $CH_3$), 4.10 (m, 6H, $OCH_2$), 6.93-7.42 (m, 3H, arom), 8.22 (s, 1H, NH), 11.24 (s, 1H, NH); *$^{13}$C-NMR* (75 MHz) 15.7 ($CH_3$), 16.0 ($CH_3$), 62.3 ($OCH_2$), 62.8 ($OCH_2$), 107.4 (d, $^1J_{PC}$= 232.6 Hz, =C-P), 126.6 (d, $^2J_{PC}$= 18.6 Hz, =C-N), 127.1-129.4 (C-arom), 153.2 (d, $^3J_{PC}$= 10.0 Hz, C=O), 155.5 (O-C=O); *$^{31}$P-NMR* (120 MHz) 4.1; *IR (KBr)* 3401, 3178, 1758, 1712, 1252, cm$^{-1}$; *MS* (EI) 389 (M$^+$, 100). Anal. Calcd for $C_{14}H_{20}N_3O_6PS$: C, 43.18; H, 5.14; N, 10.79; S, 8.22. Found: C, 42.71; H, 5.15; N, 10.97; S, 7.84.

**1-Amine Carboxylate 4-(2-furyl) 5-diethoxyphosphoryl imidazol-2-ones (5e).** 1734 mg (93 %) of **5e** as a brown solid. Data for **5e**: mp 170-171 °C; *$^1$H-NMR* (300 MHz) 1.27 (m, 9H, $CH_3$), 4.21 (m, 6H, $OCH_2$), 6.44-7.30 (m, 3H, arom), 7.99 (s, 1H, NH), 10.67 (s, 1H, NH); *$^{13}$C-NMR* (75 MHz) 14.5 ($CH_3$), 16.3 ($CH_3$), 62.7 ($OCH_2$), 63.1 ($OCH_2$), 106.2 (d, $^1J_{PC}$= 234.2 Hz, =C-P), 112.4-143.5 (C-arom), 123.9 (d, $^2J_{PC}$= 18.6 Hz, =C-N), 152.9 (d, $^3J_{PC}$= 9.7 Hz, C=O), 155.7 (O-C=O); *$^{31}$P-NMR* (120 MHz) 4.0; *IR (KBr)* 3398, 3156, 1765, 1718, 1244, cm$^{-1}$; *MS* (EI) 373 (M$^+$, 100). Anal. Calcd for $C_{14}H_{20}N_3O_7P$: C, 45.04; H, 5.36; N, 11.26. Found: C, 45.26; H, 5.41; N, 11.03.

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