Synthesis of 4-phosphazenyl-2,3-dihydropyrrol-2-ones and 5-phosphazenyl-2-pyridones from β-[(*N*-acyl)phosphazenyl]enamines and dimethyl acetylenedicarboxylate

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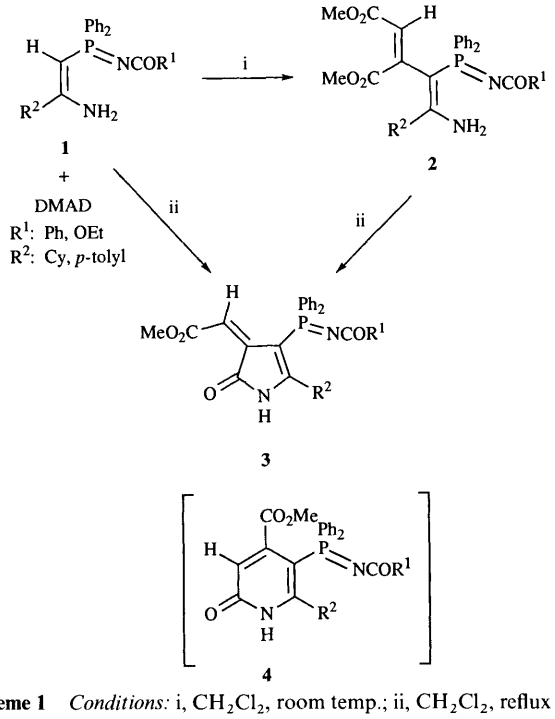
4-Phosphazenyl-2,3-dihydropyrrol-2-ones and 5-phosphazenyl-2-pyridones are obtained by addition of dimethyl acetylenedicarboxylate to [(*N*-acyl)phosphazenyl]enamines. In refluxing dichloromethane the reaction affords exclusively 2,3-dihydropyrrol-2-ones, while in toluene at 110 °C a mixture of 2-pyridones and 2,3-dihydropyrrol-2-ones is formed. They are easily separated by fractional recrystallization. The structures of all new compounds have been unequivocally assigned based on two-dimensional ^1H, ^{13}C correlation and steady-state nuclear Overhauser enhancement experiments. For 2-pyridones the absolute sign of $^4J_{PH}$ has been determined.

Introduction

We have recently shown that dimethyl acetylenedicarboxylate (DMAD) is added regio- and stereo-selectively to (*Z*)-β-enaminophosphazenes **1** in dichloromethane at room temperature[1] (Scheme 1). The products **2** obtained show the



Scheme 1 *Conditions:* i, CH_2Cl_2, room temp.; ii, CH_2Cl_2, reflux

stereochemistry of maleate, and only for R^2 = *p*-tolyl has the formation of the corresponding fumarate isomer been observed (10% in this case). However, the stereochemistry of the enamine moiety depends on the substituent R^2 present. Thus, when R^2 = *p*-tolyl (**1a**) the configuration of the starting enamine is retained in the adduct **2a** whereas for R^2 = cyclohexyl (Cy) **1b** a mixture of the *E* and *Z* isomers is identified in solution, with a relative concentration that depends on the solvent.[2]

These observations suggest that under suitable reaction conditions the isomerization of each double bond in the 1-aminobutadiene skeleton of compounds **2** might be feasible. Moreover, enamines **2** contain several functional groups of complementary reactivity, so that one may speculate on the possibility of promoting regioselective intramolecular cyclocondensations leading to different heterocyclic compounds. This would give access to heterocycles bearing a phosphorus-containing substituent, a class of potentially bioactive compounds[3] for which there are very few synthetic methods available.[4]

We have previously reported the formation of 2-pyridones when enamines **2** are refluxed in dichloromethane.[5] The structural assignment was based on chemical-shift arguments too subtle to be considered as conclusive. Therefore, we have undertaken a detailed study of the cyclocondensation of enamines **2** under different reaction conditions. The products obtained have been unequivocally identified as 4-phosphazenyl-2,3-dihydropyrrol-2-ones **3** and 5-phosphazenyl-2-pyridones **4** through the analysis of their two-dimensional ^1H, ^{13}C correlation and nuclear Overhauser enhancement (NOE) difference spectra. Consequently it is shown that the reported[5] structures for compounds **3** were incorrectly assigned.

Results and discussion

In the synthesis of the enamine derivatives **2** we noted that a small amount (< 10%) of the cyclic products **3** were formed.[1] They are only slightly soluble in CH_2Cl_2 and can be easily separated by filtration. The cyclic nature of products **3** is indicated by the loss of one equivalent of methanol in their mass and NMR spectra compared with those of the starting materials. The cyclization is made quantitative by reflux in CH_2Cl_2, of either the enaminephosphazenes **1** and DMAD or the intermediate adduct **2** (Table 1). Taking into account the isomerization capabilities of enamines **2** the products obtained may result from a 1,5- or a 1,6-cyclocondensation (Scheme 1).

For clarity the following discussion will be referred to compound **3a**. The assignment of the ^1H and ^{13}C NMR spectra is straightforward (see Experimental section). The structural elucidation was obtained from the 2D heteronuclear multiple bond coherence (HMBC)[6] spectrum measured in $(CD_3)_2SO$ ([$^2H_6$]DMSO). Thus, the NH peak at δ 11.45 shows three cross-peaks with the quaternary carbons at δ_C 160.32 ($^2J_{PC}$ 13.0 Hz), 135.70 ($^2J_{PC}$ 7.6 Hz) and 92.61 ($^1J_{PC}$ 111.2 Hz). The chemical shifts and the magnitude of the ^{31}P,^{13}C coupling constants[7] allow us to identify them as carbons C(5), C(3) and C(4), respectively of the 2-pyrrolone ring. A 2-pyridone structure is excluded because the analogous correlations of the NH group in structure **4a** would correspond to C(3), C(5) and C(6), *i.e.* a

Table 1 Mps yields and ^{31}P chemical shifts for compounds **3–6**

Compound	R^1	R^2	Mp (T/°C)	Yield (%)	$\delta(^{31}P$, ppm)
3a[a]	Ph	*p*-Tolyl	201–202	90	8.1
3b[a]	Ph	Cy	166–167	90	11.6
3c[a]	OEt	*p*-Tolyl	191–192	90	8.5
3d[a]	OEt	Cy	165–166	45	10.5
5	OEt	Cy	177–178	45	14.2
4a	Ph	*p*-Tolyl	225–226	60	26.0
4b	Ph	Cy	235–236	40	22.9
6	Ph	Cyclohexenyl	208–209	60	11.9

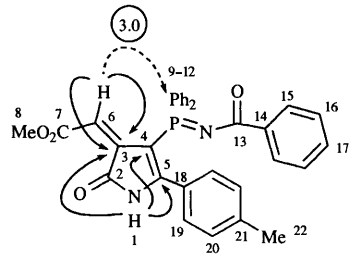
[a] Corrected structure from those reported from ref. 5.

CH carbon would be involved, what is not observed (see Figs. 1 and 3 for the labelling used). The ^1H, ^{13}C connectivity of the vinylic proton at δ 6.11 is consistent with this assignment. It also correlates with the carbons at δ_C 135.70 [C(3)] and 92.61 [C(4)] as well as the doublet at δ_C 166.90 ($^3J_{PC}$ 11.3 Hz), which is assigned to C(2). The identification of the remaining carbonyl carbons is deduced from their long-range correlations with the methyl protons for C(7) at δ_C 166.22 and with aromatic protons for C(13) at δ_C 174.59 ($^2J_{PC}$ 8.1 Hz) (Fig. 1).

Additionally, the structural assignment was confirmed by NOE difference experiments. The presaturation of the vinylic proton at δ 6.11 enhances (3%) the *ortho* protons of the *P*-phenyl rings. This information also establishes the stereochemistry of the exocyclic double bond as being *E*, *i.e.* it has retained that of the precursor **2a**.

The same study was carried out with the other members of the series, and in all cases the final product corresponded to the pyrrol-2-one heterocycle. Interestingly, the mixture of enamine isomers found for compound **2b** afford quantitatively compound **3b** when heated in CH_2Cl_2. Enamines **2c** and **d** ($R^1 = OC_2H_5$) are more reactive and already at room temperature a significant amount of pyrrol-2-ones **3c** and **d** is formed. However, by refluxing of compound **2d** ($R^1 = OC_2H_5$, R^2 = Cy) in dichloromethane a second pyrrol-2-one **5** was obtained. The relative ratio of **3**:**5** ranged from 80:20 to 40:60 on different runs probably due to variable traces of acid in the solvent.[8] Their separation was achieved by fractional recrystallization from hexane–dichloromethane. The structure was deduced from the combined use of 2D HMBC and NOE difference spectra. A key entry in the HMBC spectrum is that for the methylene protons 6-H_2 (Fig. 2). They appear as a singlet at δ 2.89 and correlate with all the carbon atoms of the pyrrol-2-one ring plus the carbonyl carbon of the adjacent CO_2Me group. On the other hand, all the methylene groups of the cyclohexylidene substituent are unequivalent. The proper connectivity is obtained through the NOEs observed when the NH signal or the *ortho* protons of the *P*-phenyl rings are presaturated. In the first case the CH_2 at δ 2.24 is enhanced, while in the second the dipolar relationship is established with the methylene protons at δ 2.33 (Fig. 2). They were then used as starting points in the assignment of the rest of the methylene signals (see Experimental section).

These results indicate that in a solvent of high relative permittivity like CH_2Cl_2 the 1,5-cyclocondensation of compounds **2** is favoured. In order to promote the isomerization of the maleate fragment of compounds **2** to the fumarate stereochemistry necessary for the 1,6-cyclization it seems reasonable that a solvent of lower polarity and/or higher boiling point should be used. The best results were obtained when enamines **2a** and **b** were heated overnight in refluxing toluene (Table 1, Scheme 2). For compound **2a** the reaction afforded a mixture of two compounds in an approximate ratio of 60:40 measured from the integral of the olefinic protons in the ^1H NMR spectrum. The ^{31}P chemical shifts are δ_P 26.0 and 8.1 for the major and minor component, respectively. They are easily separated by fractional recrystallization from hexane–



3a

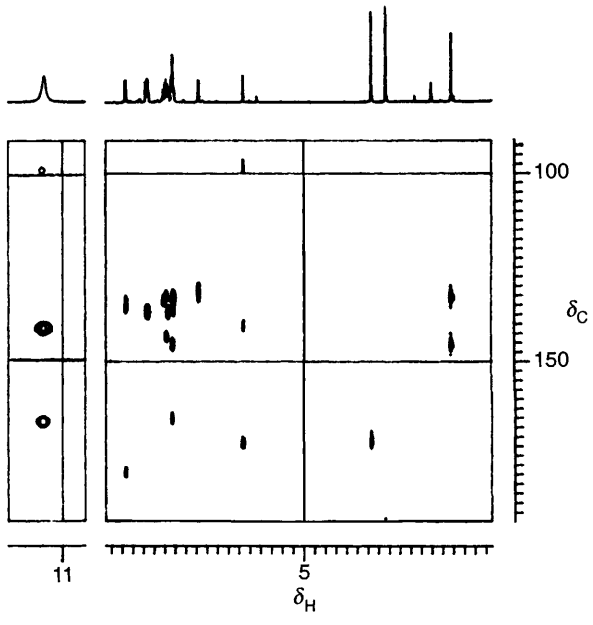


Fig. 1 400 MHz 2D HMBC spectrum of compound **3a** in [$^2H_6$]DMSO. Continuous arrows on the formula correspond to key correlations discussed in the text. Selected NOEs are indicated by dashed arrows, and circled figures express the percentage of enhancement. The labelling used in the assignment is included.

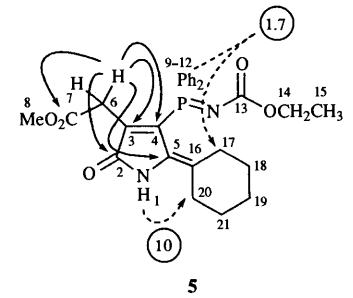


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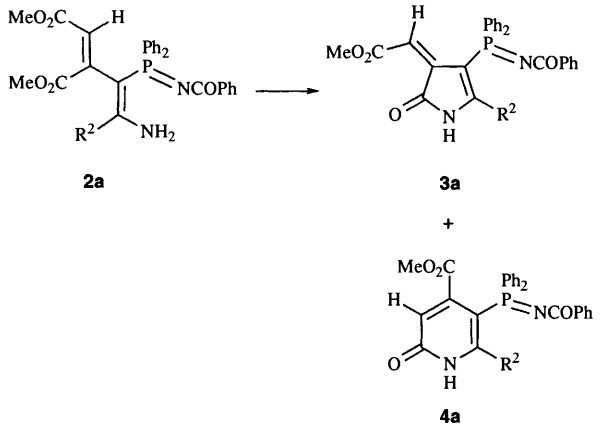
Fig. 2 Selected ^1H, ^{13}C HMBC correlations (continuous arrows) and NOEs (dashed arrows, circled figures express the percentage of enhancement) observed for the 2-pyrrolone **5**. The numbering scheme used is also indicated.



Scheme 2 *Conditions:* toluene, reflux

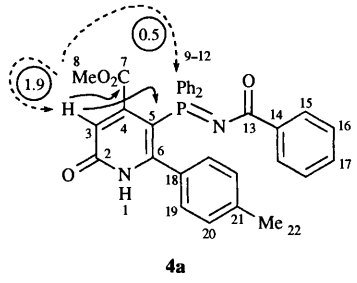


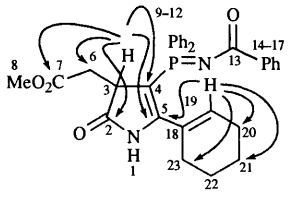
Fig. 3 Selected ^{1}H, ^{13}C HMBC correlations (continuous arrows) and NOEs (dashed arrows, circled figures express the percentage of enhancement) observed for the 2-pyrrolone **4a**. The numbering scheme used is also indicated.

dichloromethane. The compound with δ_P 8.1 corresponds to the pyrrol-2-one **3a** already identified. The new product was identified as the 2-pyridone **4a** on the basis of ^{1}H, ^{13}C correlations and NOE data.

The olefinic proton H(3) appears as a doublet at δ 6.92 ($^{4}J_{PH}$ 2.5 Hz). In the HMBC spectrum it shows two cross-peaks with the carbons at δ_C 166.78 and 102.0 ($^{1}J_{PC}$ 110.0 Hz), which are readily assigned to C(7) and C(5), *i.e.*, the carbon atoms separated from H(3) by three bonds. It is well known that, usually, $^{3}J_{CH} > {}^{2}J_{CH}$ so that ^{1}H, ^{13}C correlations for nuclei separated by three bonds are more easily detected than those mediating two bonds.[9] Unfortunately, the large linewidth of the NH signal precluded the observation of any correlation probably due to rapid relaxation of the second kind.[10] Additional support for the structure proposed was obtained from NOE experiments. The presaturation of the methoxy group enhanced the signal of H(3) and the *ortho* protons of the *P*-phenyl rings (Fig. 3).

When compound **2b** was heated in toluene for 12 h a mixture of two compounds **4b** and **6** in the ratio 40:60, was obtained; compound **3b** was not detected by NMR spectroscopy in the reaction crude product. The respective ^{31}P chemical shifts are δ_P 11.9 and 22.9 (Table 1, Fig. 4). Fractional recrystallization from hexane–dichloromethane allows their separation and identification. The structure of 2-pyridone **4b** was assigned by analogy with the analysis previously discussed for compound **4a**.

Significantly, the ^{1}H NMR spectrum of compound **6** presents an AB quartet for the methylene protons adjacent to the CO_2Me group, which are further coupled to a vicinal proton and to a phosphorus through four bonds. In the HMBC spectrum the correlations of the proton at δ 3.97 [H(3)] define completely the structure of the 2,3-dihydropyrrol-2-one ring and the position of the CH_2CO_2Me fragment. They are indicated in Fig. 4 by arrows, as are those of the olefinic proton used to assign the methylene protons of the cyclohexenyl substituent. Therefore, the cyclocondensation of compound **2b** in toluene proceeds in a similar way to that of compound **2a** except that



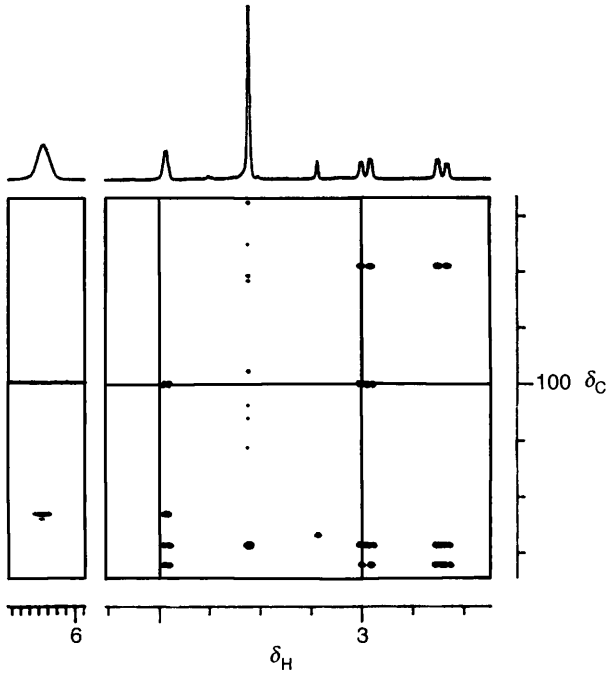


Fig. 4 Section of the 2D HMBC spectrum of compound **6** corresponding to the aliphatic region of the ^{1}H NMR spectrum. Key correlations are indicated by arrows (see text for the assignments). The molecular formula shows the atom-labelling used.

under the reaction conditions the expected pyrrolone **3b** is unstable and rearranges to the isomer **6**.

An interesting point arising from pyridones **4a** and **b** is the $^{4}J_{PH}$ coupling observed for H(3). We have previously shown[1] that in allylic systems $^{4}J_{PH}$ behaves analogously to $^{4}J_{HH}$ and $^{4}J_{CH}$, *i.e.* it can be considered as the sum of a positive, J^{σ} and a negative J^{π} contribution,[11] where $^{4}J^{\pi}_{PH}$ exhibits a $\cos^2\varphi$ dependence, φ being the angle formed between the sp^3 hybridized C–P bond and the axis of the adjacent $2p_{\pi}$ orbital (Fig. 5).[12] For compounds **4** this angle is forced by the ring to be 90° and therefore the J^{π} contribution to $^{4}J_{PH}$ should be vanishing small. Consequently, the σ component must predominate and $^{4}J_{PH}$ should be positive. This was experimentally confirmed by the HMBC spectra of pyridones **4**. The cross-peak correlating H(3) with C(5) showed a positive slope, thus indicating that the passive couplings $^{4}J_{PH}$ and $^{1}J_{PC}$ have same relative signs.[1,13] Since a positive sign[14] can be assumed for $^{1}J_{PC}$ it can be concluded that $^{4}J_{PH}$ is positive. As far as we know this is the first experimental determination of a positive $^{4}J_{PH}$ coupling in allylic fragments.

As mentioned above, enamines **1c** and **d** are too reactive to allow isolation of the compounds **2c** and **d** because they transform rapidly into dihydropyrrolones **3c** and **d** during the manipulation. As an alternative to obtaining the corresponding 2-pyridones we tried the direct reaction between enamines **1c** and **d** and DMAD in refluxing toluene. Instead, we obtained quantitatively the 1-aza-4λ^5-phosphinines **7**, a compound-class already characterized in the reaction of aminoarylenaphosphazenes and DMAD in tetrahydrofuran (THF) (Scheme 3).[15] They result from the [2+2] addition of DMAD to the P=N double bond[16] followed by ring opening and cycloconden-

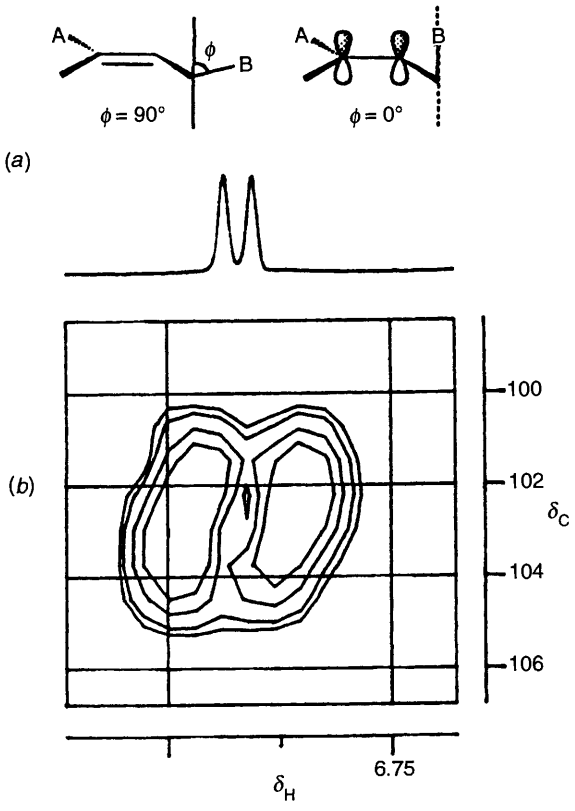
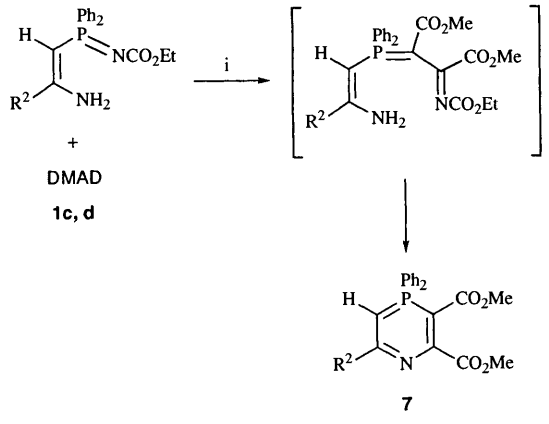


Fig. 5 (*a*) Dependence of the J^{π} contribution to $^4J_{PH}$ on angle ϕ. (*b*) Cross-peak corresponding to the correlation of H(3) with C(5) in the 2D HMBC spectrum of compound **4a**. From its slope a positive $^4J_{PH}$ is assigned (*cf.* ref. 1).



Scheme 3 *Conditions:* toluene, reflux

sation. This process do not occur with the *N*-benzoylderivatives **1a** and **b** because of the extended conjugation of the P=N moiety with the benzoyl group.[17]

In summary, the addition of DMAD to [(*N*-acyl)phosphazenyl]enamines affords 2-pyrrolones and 2-pyridones depending on the reaction conditions. The five-membered heterocycles are formed regioselectively in almost quantitative yields in refluxing dichloromethane, while 2-pyridones are obtained in moderate yields together with some 2-pyrrolone isomer when the reaction is performed in toluene at 110 °C. Fortunately, the mixtures are easily separated by fractional recrystallization. Their structures have been unequivocally assigned by the combined use of ^{1}H, ^{13}C correlation and NOE difference spectra. Pyrrolones with R^2 = Cy showed a marked tendency to isomerization so that three different compounds have been characterized. In all cases the integrity of the 2-pyrrolone ring is maintained, and the isomers derive from 1,5-proton shifts involving the cyclohexyl substituent. For 2-pyridones a positive $^4J_{PH}$ has been characterized for the first time.

Experimental

General

Compounds **2** and **3** have been synthesized according to literature methods.[5] Microanalyses were performed on a Perkin-Elmer 240 B Instrument. Mps were measured in a Büchi-Tottoli apparatus and are uncorrected. IR spectra were recorded on a FTIR Mattson 3020 spectrophotometer. Mass spectra were obtained on a Hewlett-Packard 5987A. NMR spectra were recorded on Bruker AMX400 and AC300 spectrometers. Spectra were obtained with deuteriated chloroform as solvent. Chemical shifts are reported δ-units, downfield from internal $SiMe_4$ for ^{1}H and ^{13}C NMR and from H_3PO_4 (85%) in the case of ^{31}P NMR spectra. *J* Values are given in Hz. Standard experimental parameters for the acquisition of NOE difference spectra were used. The proton-detected heteronuclear 2D correlation experiments were acquired with 256 time increments and zero filled to give a final 2048 × 1024 data matrix. The reported structures for compounds **3** are incorrect; therefore, the full assignment of the ^{1}H and ^{13}C NMR spectra of these compounds is included.[5]

Synthesis of 2-pyrrolones 3, 5 and 6

A solution of compounds **2a–d** (5 mmol) in dry CH_2Cl_2 was heated 12 h at reflux. Evaporation of the mixture under reduced pressure afforded a crude solid, which was recrystallized from hexane–dichloromethane to give compounds **3**, **5** and **6**.

Methyl (*E*)-{4-[benzoylimino(diphenyl)-λ^5-phosphanyl]-2-oxo-5-(*p*-tolyl)-2,3-dihydropyrrol-3-ylidene}acetate 3a. (90%), Mp 201–202 °C; ν_{max}(KBr)/cm^{-1} 3180 (NH), 1740, 1730, 1720 (C=O) and 1360 (P=N); δ_H(400.13 MHz; [$^2H_6$]DMSO) (refer to Fig. 1 for numbering scheme) 2.23 (3 H, s, 22-H_3), 3.73 (3 H, s, 8-H_3), 6.11 (1 H, s, 6-H), 6.93–6.95 (2 H, m, 2 × 20-H), 7.41–7.46 (6 H, m, 4 × 11-H and 2 × 12-H), 7.51–7.58 (5 H, m, 2 × 16-H, 17-H and 2 × 19-H), 7.89–7.94 (4 H, m, 4 × 10-H), 8.31–8.34 (2 H, m, 2 × 15-H) and 11.45 (1 H, s, 1-H); δ_C(100.62 MHz; [$^2H_6$]DMSO) 20.91 (C-22), 51.98 (C-8), 92.61 (d, $^1J_{PC}$ 111.2, C-4), 125.74 (C-6), 125.96 (d, $^3J_{PC}$ 2.1, C-18), 127.83 (C-20), 127.98 (C-16), 128.54 (d, $^3J_{PC}$ 12.6, C-11), 128.84 (C-19), 129.00 (C-12), 129.06 (C-16), 131.27 (d, $^1J_{PC}$ 104.6, C-9), 131.78 (C-15), 132.11 (d, $^2J_{PC}$ 9.8, C-10), 135.70 (d, $^2J_{PC}$ 7.6, C-3), 138.47 (d, $^3J_{PC}$ 20.5, C-14), 140.65 (C-21), 160.32 (d, $^2J_{PC}$ 13.0, C-5), 166.22 (C-7), 166.90 (d, $^3J_{PC}$ 11.3, C-2) and 174.59 (d, $^2J_{PC}$ 8.1, C-13); δ_P(121.4 MHz; [$^2H_6$]DMSO) 7.2; δ_P(121.4 MHz; $CDCl_3$) 8.

Methyl (*E*)-{4-[benzoylimino(diphenyl)-λ^5-phosphanyl]-5-cyclohexyl-2-oxo-2,3-dihydropyrrol-3-ylidene}acetate 3b. (90%), Mp 166–167 °C; ν_{max}(KBr)/cm^{-1} 3100 (NH), 1740, 1640, 1600 (C=O) and 1350 (P=N); δ_H(300.13 MHz; $CDCl_3$) 0.65 (2 H, s, 20-H_2), 1.10 (3 H, m, 19-H and 21-H_2), 1.50 (5 H, m, 3 × 19-H and 20-H_2), 2.27 (1 H, m, 18-H), 3.71 (3 H, s, 8-H_3), 6.20 (1 H, s, 6-H), 7.40–7.60 (9 H, m, 2 × 16-H, 17-H, 4 × 11-H and 2 × 12-H), 7.98–8.03 (4 H, m, 4 × 10-H), 8.23–8.30 (2 H, m, 2 × 15-H) and 8.9 (1 H, s, 1-H); δ_C(75.5 MHz; [$^2H_6$]DMSO) 24.82 (C-19), 25.33 (C-20), 28.60 (C-21), 37.56 (C-18), 52.14 (C-8), 92.09 (d, $^1J_{PC}$ 119.0, C-4), 123.96 (C-6), 127.94 (C-16), 129.06 (C-15), 129.23 (d, $^1J_{PC}$ 104.7, C-9), 129.33 (d, $^3J_{PC}$ 12.2, C-11), 130.85 (C-17), 132.4 (d, $^2J_{PC}$ 10.1, C-10), 132.87 (C-12), 135.16 (d, $^2J_{PC}$ 8.2, C-3), 138.73 (d, $^3J_{PC}$ 20.2, C-14), 166.47 (C-7), 167.36 (d, $^2J_{PC}$ 19.5, C-2), 167.42 (d, $^2J_{PC}$ 5.9, C-5) and 174.62 (d, $^2J_{PC}$ 8.0, C-13); δ_P(121.4 MHz; [$^2H_6$]DMSO) 10.3; δ_P(121.4 MHz; $CDCl_3$) 11.6.

Methyl (*E*)-{4-[ethoxycarbonylimino(diphenyl)-λ^5-phosphanyl]-2-oxo-5-(*p*-tolyl)-2,3-dihydropyrrol-3-ylidene}acetate 3c. (90%), Mp 191–192 °C; ν_{max}(KBr)/cm^{-1} 3256 (NH), 1742, 1648 (C=O) and 1393 (P=N); δ_H(300.13 MHz; $CDCl_3$) 2.18 (3 H, s, 20-H_3), 3.64 (3 H, s, 8-H_3), 6.12 (1 H, s, 6-H), 6.80–6.83 (2 H, m, 2 × 18-H), 7.24–7.36 (8 H, m, 2 × 17-H, 4 × 11-H and 2 × 12-H), 7.67–7.74 (4 H, m, 4 × 10-H) and 9.24 (1 H, s, 1-H); δ_C(75.5 MHz; [$^2H_6$]DMSO) 14.80 (C-15), 20.92 (C-20), 51.99

(C-8), 60.36 (d, $^4J_{PC}$ 3.2, C-14), 93.21 (d, $^1J_{PC}$ 112.3, C-4), 125.62 (C-6), 125.82 (C-16), 127.96 (C-18), 128.47 (d, $^3J_{PC}$ 12.2, C-11), 128.65 (d, $^1J_{PC}$ 119.9, C-9), 128.69 (C-12), 131.75 (C-17), 131.84 (d, $^2J_{PC}$ 9.8, C-10), 135.67 (d, $^2J_{PC}$ 7.6, C-3), 140.63 (C-19), 160.42 (d, $^2J_{PC}$ 13.1, C-5), 161.10 (C-13), 166.19 (C-7) and 166.83 (d, $^3J_{PC}$ 10.9, C-2); δ_P(121.4 MHz; $CDCl_3$) 8.5.

Methyl (*E*)-{5-cyclohexyl-4-[ethoxycarbonylimino(diphenyl)-λ^5-phosphanyl]-2-oxo-2,3-dihydropyrrol-3-ylidene}acetate 3d. (45%), Mp 165–166 °C; ν_{max}(KBr)/cm^{-1} 3100 (NH), 1737, 1627 (C=O) and 1438 (P=N); δ_H(300.13 MHz; $CDCl_3$) 0.7–0.9 (2 H, m, 19-H_2), 1.0–1.4 (4 H, m, 17-H_2), 1.3 (3 H, t, $^3J_{HH}$ 7.1, 15-H_3), 1.45–1.70 (4 H, m, 18-H_2), 2.10–2.25 (1 H, m, 16-H), 3.73 (3 H, s, 8-H_3), 4.1 (2 H, q, $^3J_{HH}$, 14-H_2), 6.2 (1 H, s, 6-H), 7.4–7.7 (6 H, m, 4 × 11-H and 2 × 12-H), 7.8–8.0 (4 H, m, 4 × 10-H) and 9.6 (1 H, s, 1-H); δ_C(75.5 MHz; $CDCl_3$) 14.80 (C-15), 25.10 (C-19), 25.38 (C-17), 29.38 (C-18), 37.23 (C-16), 52.08 (C-8), 61.21 (d, $^4J_{PC}$ 3.6, C-14), 93.80 (d, $^1J_{PC}$ 117.8, C-4), 126.74 (C-6), 128.84 (d, $^1J_{PC}$ 108.3, C-9), 128.91 (d, $^3J_{PC}$ 12.7, C-11), 132.53 (d, $^2J_{PC}$ 7.6, C-10), 132.64 (d, $^4J_{PC}$ 2.2, C-12), 134.91 (d, $^2J_{PC}$ 7.6, C-3), 162.04 (C-13), 165.70 (d, $^2J_{PC}$ 15.4, C-5), 166.48 (C-7) and 168.17 (d, $^3J_{PC}$ 11.4, C-2); δ_P(121.4 MHz; $CDCl_3$) 10.5.

Methyl (*E*)-5-cyclohexylidene-{4-[Ethoxycarbonylimino-(diphenyl)-λ^5-phosphanyl]-2-oxo-2,5-dihydropyrrol-3-yl}acetate 5. (45%), Mp 177–178 °C; ν_{max}(KBr)/cm^{-1} 3258 (NH), 1728, 1702 (C=O) and 1373 (P=N); δ_H(300.13 MHz; $CDCl_3$) (see Fig. 2 for numbering scheme) 0.78 (2 H, m, 18-H_2), 1.29 (2 H, m, 19-H_2), 1.18 (3 H, t, $^3J_{HH}$ 7.1, 15-H_3), 1.47 (2 H, m, 21-H_2), 2.24 (2 H, m, 20-H_2), 2.33 (2 H, m, 17-H_2), 2.89 (2 H, s, 6-H_2), 3.40 (3 H, s, 8-H_3), 4.05 (2 H, q, $^3J_{HH}$ 7.1, 14-H_2), 7.37–7.50 (6 H, m, 4 × 11-H and 2 × 12-H), 7.72–7.80 (4 H, m, 4 × 10-H) and 10.16 (1 H, s, 1-H); δ_C(100.62 MHz; $CDCl_3$) 14.76 (C-15), 25.75 (C-19), 26.95 (C-18), 27.93 (C-21), 30.57 (C-20), 30.58 (C-6), 30.59 (C-17), 51.69 (C-8), 61.32 (d, $^4J_{PC}$ 3.5 Hz, C-14), 128.82 (d, $^3J_{PC}$ 13.0, C-11), 128.90 (d, $^1J_{PC}$ 109.8, C-9), 130.18 (d, $^2J_{PC}$ 12.9, C-5), 130.29 (d, $^1J_{PC}$ 89.0, C-4), 132.36 (d, $^2J_{PC}$ 10.2, C-10), 132.61 (d, $^4J_{PC}$ 2.6, C-12), 137.09 (C-16), 143.67 (d, $^2J_{PC}$ 6.2, C-3), 162.12 (d, $^2J_{PC}$ 1.5, C-13), 168.56 (d, $^3J_{PC}$ 17.4, C-2) and 169.64 (d, $^4J_{PC}$ 1.0, C-7); δ_P(121.4 MHz; $CDCl_3$) 14.2; *m*/*z* 506 (M^+, 10%), 433 (25), 201 (42) and 32 (100) (Found: C, 66.4; H, 6.1; N, 5.6; P, 6.1. $C_{28}H_{31}N_2O_5P$ requires C, 66.38; H, 6.17; N, 5.53; P, 6.12%).

Synthesis of 2-pyridones 4

A solution of a compound **2a–d** (5 mmol) in dry toluene was heated for 12 h at reflux. Evaporation of the mixture under reduced pressure afforded a crude solid. Fractional recrystallization from hexane–dichloromethane afforded 2,3-dihydropyrrol-2-ones. The mother liquor was concentrated under reduced pressure and then recrystallized from hexane–toluene to give compounds **4**.

Methyl 5-[benzoylimino(diphenyl)-λ^5-phosphanyl]-2-oxo-6-(*p*-tolyl)-2,3-dihydropyridine-4-carboxylate 4a. (40%), Mp 225–226 °C, ν_{max}(KBr)/cm^{-1} 3430 (NH), 1730, 1659 (C=O) and 1339 (P=N); δ_H(300.13 MHz; $CDCl_3$) (Fig. 3 refers for numbering scheme) 2.02 (3 H, s, 22-H_3), 3.65 (3 H, s, 8-H_3), 6.61–6.70 (2 H, m, 2 × 20-H), 6.75–6.85 (2 H, m, 2 × 19-H), 6.92 (1 H, d, $^4J_{PH}$ 2.5, 3-H), 7.30–7.55 (9 H, m, 2 × 16-H, 17-H, 4 × 11-H and 2 × 12-H), 7.80–7.90 (4 H, m, 4 × 10-H), 7.90–8.00 (2 H, m, 2 × 15-H) and 11.34 (1 H, s, NH); δ_C(100.61 MHz; $CDCl_3$) 21.16 (C-22), 52.37 (C-8), 102.0 (d, $^1J_{PC}$ 110.0, C-5), 120.86 (d, $^3J_{PC}$ 6.4, C-3), 127.53 (d, $^3J_{PC}$ 5.1, C-18), 128.06 (d, $^3J_{PC}$ 12.7, C-11), 128.41 (C-16), 128.97 (C-20), 129.36 (d, $^4J_{PC}$ 1.9, C-15), 129.90 (d, $^1J_{PC}$ 97.9, C-9), 130.33 (C-12), 131.76 (C-17), 131.79 (C-19), 133.42 (d, $^2J_{PC}$ 10.1, C-10), 138.37 (d, $^3J_{PC}$ 21.6, C-14), 140.59 (C-21), 148.92 (d, $^2J_{PC}$ 6.0, C-4), 156.58 (d, $^2J_{PC}$ 17.8, C-6), 162.31 (C-2), 166.78 (C-7) and 174.71 (d, $^2J_{PC}$ 7.6, C-13); δ_P(121.4 MHz; $CDCl_3$) 26.0; *m*/*z* 578 (M^+, <1%), 519 (9), 384 (39) and 201 (100) (Found: C, 71.8; H, 4.9; N, 5.2; P, 5.6. $C_{33}H_{27}N_2O_4P$ requires C, 72.5; H, 4.98; N, 5.13; P, 5.67%).

Methyl 5-[benzoylimino(diphenyl)-λ^5-phosphanyl]-6-cyclohexyl-2-oxo-2,3-dihydropyridine-4-carboxylate 4b. (40%), Mp 235–236 °C, ν_{max}(KBr)/cm^{-1} 3370 (NH), 1726, 1682 (C=O) and 1352 (P=N); δ_H(400.13 MHz $CDCl_3$) 0.60 (2 H, m, 21-H_2), 1.10–1.60 (8 H, m, 2 × 19-H_2 and 2 × 20-H_2), 3.08 (1 H, m, 18-H), 3.22 (3 H, s, 8-H_3), 6.71 (1 H, d, $^4J_{PH}$ 2.8, 3-H), 7.38–7.41 (3 H, m, 17-H and 16-H), 7.55–7.58 (6 H, m, 4 × 11-H and 2 × 12-H), 8.12 (4 H, m, 4 × 10-H) and 8.22 (2 H, m, 2 × 15-H); δ_C(100.62 MHz; $CDCl_3$) 24.86 (C-21), 25.84 (C-20), 30.09 (C-19), 42.56 (C-18), 52.37 (C-8), 101.48 (d, $^1J_{PC}$ 114.4, C-5), 119.18 (d, $^3J_{PC}$ 7.9, C-3), 127.62 (C-16), 128.67 (d, $^3J_{PC}$ 13.0, C-11), 129.07 (d, $^1J_{PC}$ 97.4, C-9), 129.43 (d, $^4J_{PC}$ 2.4, C-15), 130.56 (C-17), 132.42 (d, $^4J_{PC}$ 2.7, C-12), 133.24 (d, $^2J_{PC}$ 10.7, C-10), 138.31 (d, $^3J_{PC}$ 21.4, C-14), 148.87 (d, $^2J_{PC}$ 6.8, C-4), 162.41 (d, $^2J_{PC}$ 17.4, C-6), 163.66 (C-2), 167.02 (d, $^3J_{PC}$ 1.7, C-7) and 176.00 (d, $^2J_{PC}$ 8.0, C-13); δ_P(121.4 MHz; $CDCl_3$) 22.9; *m*/*z* 524 (M^+ − 15, < 1%), 420 (6), 342 (1), 200 (19), 105 (5) and 40 (100) (Found: C, 71.5; H, 5.9; N, 5.1; P, 5.7. $C_{32}H_{31}N_2O_4P$ requires C, 71.35; H, 5.8; N, 5.2; P, 5.76%).

Methyl {4-[benzoylimino(diphenyl)λ^5-phosphanyl]-5-(cyclohex-1-enyl)-2-oxo-2,3-dihydropyrrol-3-yl}acetate 6. (60%), Mp 208–209 °C; ν_{max}(KBr)/cm^{-1} 3435 (NH), 1736, 1726 (C=O) and 1346 (P=N); δ_H(300.13 MHz; $CDCl_3$) (refer to Fig. 4 for numbering scheme) 0.9–1.98 (8 H, m, $CyCH_2$s), 2.42 (1 H, AB, $^2J_{HH}$ 17.8, $^3J_{HH}$ 4.2, 6-H), 3.16 (1 H, AB, $^2J_{HH}$ 17.8, $^3J_{HH}$ 5.1 6-H), 3.55 (3 H, s, 8-H_3), 3.97 (1 H, m, 3-H), 6.08 (1 H, m, 19-H), 7.40–7.60 (9 H, m, 4 × 11-H, 2 × 12-H, 2 × 16-H and 17-H), 7.88–7.95 (2 H, m, 2 × 10-H), 8.01–8.08 (2 H, m, 2 × 10-H), 8.29–8.31 (2 H, m, 2 × 15-H) and 8.55 (1 H, s, 1-H); δ_C(100.61 MHz; $CDCl_3$) 20.55 (C-21), 21.42 (C-22), 24.82 (C-23), 26.09 (C-20), 33.28 (C-6), 47.05 (d, $^2J_{PC}$ 7.52, C-3), 51.56 (C-8), 99.52 (d, $^1J_{PC}$ 113.7, C-4), 126.98 (d, $^3J_{PC}$ 10.2, C-18), 127.64 (C-16), 128.59 (d, $^3J_{PC}$ 12.6, C-11), 128.64 (d, $^3J_{PC}$ 12.5, C-11), 129.33 (d, $^4J_{PC}$ 2.3, C-15), 130.49 (d, $^1J_{PC}$ 91.2, C-9), 130.58 (C-17), 131.91 (d, $^4J_{PC}$ 2.6, C-12), 132.16 (d, $^4J_{PC}$ 2.6, C-12), 132.48 (d, $^2J_{PC}$ 10.1, C-10), 132.71 (d, $^2J_{PC}$ 10.2, C-10), 135.88 (C-19), 138.77 (d, $^3J_{PC}$ 15.3, C-14), 157.66 (d, $^2J_{PC}$ 15.3, C-5), 171.36 (C-7), 175.56 (d, $^2J_{PC}$ 18.4, C-13) and 180.74 (d, $^3J_{PC}$ 12.2, C-2); δ_P(121.4 MHz; $CDCl_3$) 11.9; *m*/*z* 538 (M^+, > 3%), 236 (2), 200 (63) and 77 (100) (Found: C, 72.0; H, 5.8; N, 5.15; P, 5.85. $C_{32}H_{31}N_2O_4P$ requires C, 71.35; H, 5.80; N, 5.20; P, 5.76%).

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