# Heterocyclization Reactions of Conjugated Heterocumulenes. Synthesis of Pyridine Derivatives by a Tandem Aza Wittig/Electrocyclization Strategy[1)]

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The aza Wittig reaction of iminophosphorane **3** with isocyanates leads to conjugated carbodiimides **4**, which undergo electrocyclic ring closure to give ethyl 2-pyridinecarboxylates **5**. Iminophosphorane **9** reacts with nitromethane and acetone in a 1:1 molar ratio to form **10** and **11**, respectively. Reaction of **9** with nitromethane in 1:3 molar ratio yields the iminophosphorane **12**. The structure of **12** has been established by X-ray crystallography. Iminophosphoranes **10** and **11** react with isocyanates or carbon dioxide to give the pyrazolo[3,4-*b*]pyridines **13**, **15** and **14**, **16**, respectively.

**Cyclisierungsreaktionen von konjugierten Heterocumulenen. Synthese von Pyridinderivaten durch Tandem-Aza-Wittig/Elektro-Ringschluß-Strategie**

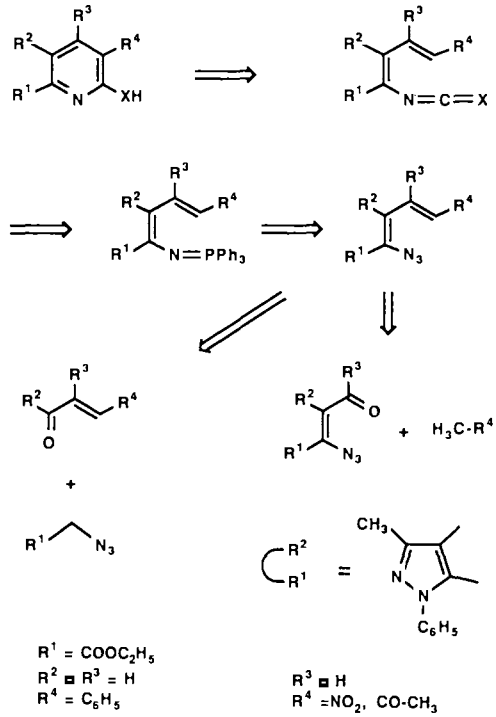
Die Aza-Wittig-Reaktion der Iminophosphorane **3** mit Isocyanaten führt zu konjugierten Carbodiimiden **4**, die elektrocyclisch 2-Pyridincarbonsäureester **5** ergeben. Iminophosphoran **9** reagiert mit Nitromethan bzw. Aceton im Molverhältnis 1:1 zu **10** bzw. **11**. Aus **9** und Nitromethan 1:3 entsteht das Iminophosphoran **12**. Dessen Struktur wurde durch Kristallstrukturanalyse bewiesen. Die Iminophosphorane **10**, **11** reagieren mit Isocyanaten oder Kohlendioxid zu den Pyrazolo[3,4-*b*]pyridinen **13**, **15** bzw. **14**, **16**.

It has become increasingly apparent that α,β-unsaturated heterocumulenes are highly useful as synthetic intermediates in preparative heterocyclic chemistry. Especially cycloaddition reactions of such unsaturated heterocumulenic systems as, e.g., ketenes, isocyanates, isothiocyanates, and ketene imines provide an attractive entry to a variety of heterocycles[2)]. However, relatively few examplex of thermally induced 6π electrocyclizations of conjugated heterocumulenes have been documented[3)]; only the thermal cyclization of (β-heteroaryl)vinylcarbodiimides[4)], styrylcarbodiimides[5)], styryl isocyanates[6)], β-carbamoylvinyl isocyanates[7)], and β-substituted vinyl ketenes[8)] have been mentioned.

On the other hand, the aza Wittig reaction of iminophosphoranes with heterocumulenes, e.g. carbon dioxide, carbon disulfide, and isocyanates or isothiocyanates, is a very useful reaction in synthetic heterocyclic chemistry[9)]. Consequently, improvements which increase the efficiency or enlarge its applicability are always desirable, and the discovery of novel functionalized iminophosphoranes bearing a moiety able to react with the aza Wittig product is important in this respect.

Continuing our interest in the iminophosphorane-mediated synthesis of heterocycles, we describe a simple and apparently general procedure for the synthesis of conjugated heterocumulenes and the first synthesis of pyridine derivatives by electrocyclic ring closure of conjugated carbodiimides, isothiocyanates, and isocyanates.

Our approach is centered on the aza Wittig reaction of iminophosphoranes with heterocumulenes to give a 1,3,5-hexatriene moiety containing cumulated double bonds at one end, which subsequently undergo electrocyclic ring closure to yield the cyclic valence tautomer pyridine ring. The preparation of the desired iminophosphoranes is accomplished very easily through the classical Staudinger reaction of triphenylphosphane with vinyl azides, the latter ones being readily available either from α,β-unsaturated aldehydes and ethyl azidoacetate or from azidoformylazoles and activated methylene compounds.




## Results and Discussion

Electrocyclization of acyclic molecules to give a pyridine ring, involving formation of a single bond β to the nitrogen atom, has

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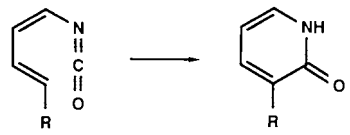
been little investigated as a synthetic route. It has only been reported that 1,3-dieneacyl azide[10] and propargylic pyrrolodine pseudoureas[11] by thermolysis lead to substituted 2(1*H*)-pyridinones, presumably by an electrocyclic ring closure of a (1*Z*)-1,3-diene isocyanate intermediate **1**. In each case the isocyanate was not directly observed. Although this 2(1*H*)-pyridinone synthesis has not been extensively explored, it would appear limited mainly by the availability of the starting materials.



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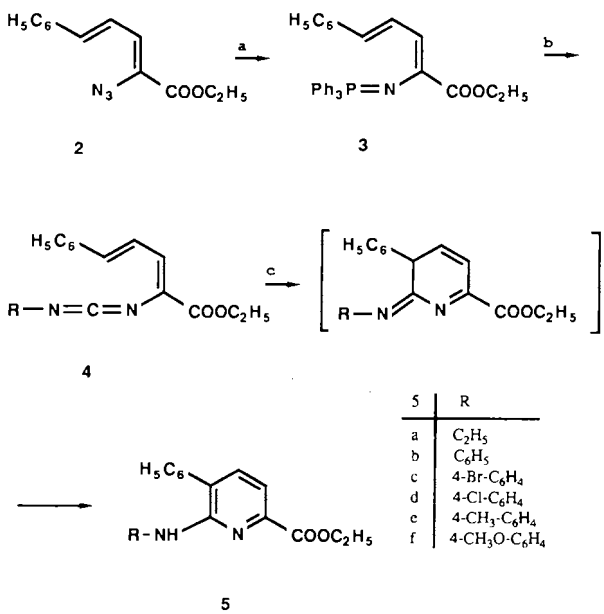
We report here a useful method for the synthesis of C=C conjugated carbodiimides by an aza Wittig reaction of iminophosphorane **3** with isocyanates and the first general synthesis of pyridine derivatives based on the electrocyclic ring closure of carbodiimides **4**. The preparation of **4** is accomplished easily by the Staudinger reaction of ethyl 2-azido-5-phenyl-2,4-butadienecarboxylate (**2**) (readily available from cinnamaldehyde and ethyl azidoacetate[12]), with triphenylphosphane in dry dichloromethane at room temperature giving the iminophosphorane **3**. Aza Wittig reaction of **3** with isothiocyanates in dry toluene at room temperature leads to the corresponding carbodiimides **4**, which could be isolated as viscous oils by means of short-column chromatography. Upon heating in dry toluene, compounds **4** undergo an electrocyclic ring closure followed by a 1,3-proton shift to give the otherwise not readily available ethyl 6-[alkyl(aryl)amino]-5-phenyl-2-pyridinecarboxylates **5** in good yields. Similar results are obtained when iminophosphorane **3** and the appropriate isothiocyanate are heated in dry toluene at reflux temperature for 12 h.



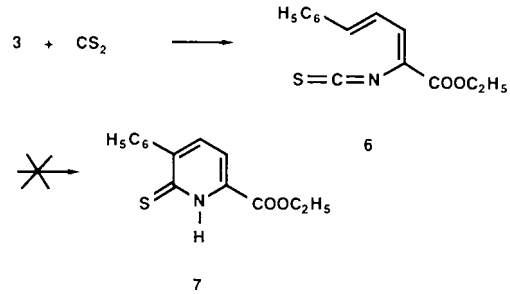
| 5 | R |
|---|---|
| a | $C_2H_5$ |
| b | $C_6H_5$ |
| c | 4-Br-$C_6H_4$ |
| d | 4-Cl-$C_6H_4$ |
| e | 4-$CH_3$-$C_6H_4$ |
| f | 4-$CH_3O$-$C_6H_4$ |

2 3 4 5

a: $Ph_3P/CH_2Cl_2$/room temp.; b: RNCS/toluene/room temp.; c: heat/toluene

On the other hand, iminophosphorane **3** reacts with carbon disulfide to give the isothiocyanate **6** as yellow crystalline solid in 73% yield. In solution under thermolysis conditions **6** does not undergo cyclization to the desired 2(1*H*)-pyridinethione **7**.

Electron-impact mass spectra of compounds **5** show the expected molecular ion peaks in high intensity, and the IR spectra exhibit N–H absorption bands at 3440–3415 $cm^{-1}$. The absence of carbodiimide bands provides support for the formulation as **5**. The $^1$H-NMR spectra suggest the exocyclic NH of **5**; e.g. for **5a** the methylene signal appears as a complex multiplet.

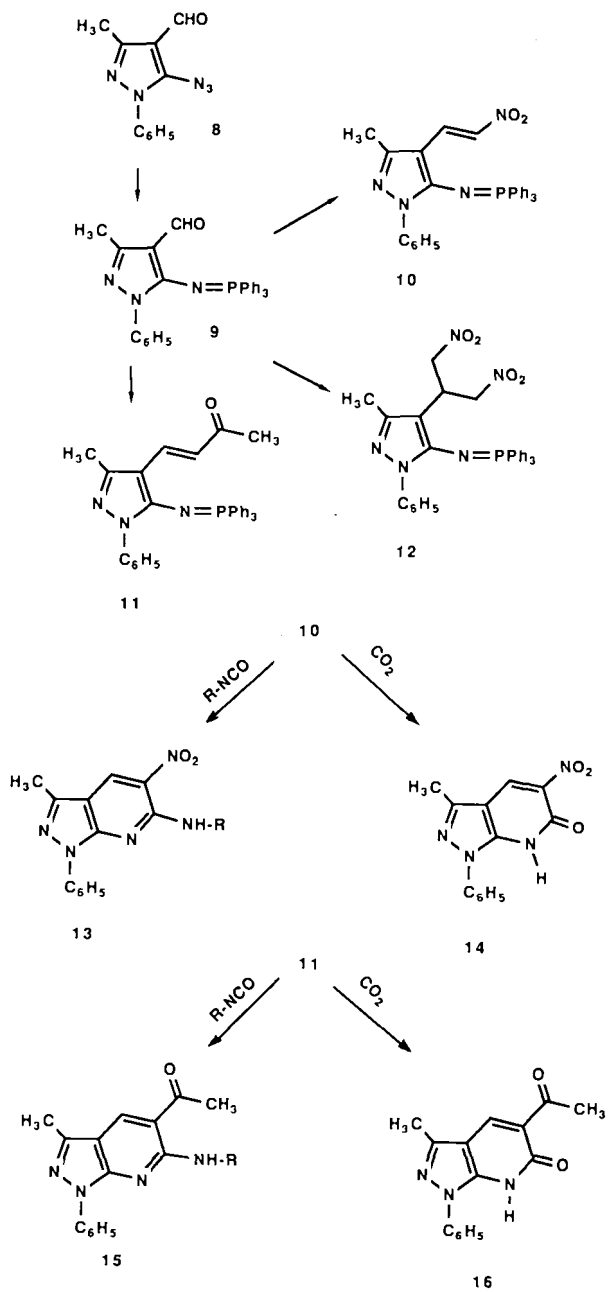


6 7

Pyrazolo[3,4-*b*]pyridines have received considerable attention as a result of their biological activity and structural relationship to indoles, and several methods have been adopted for the synthesis of this ring system and have been comprehensively reviewed[13]. Reaction of 3-aminopyrazole derivatives with 1,3-dicarbonyl compounds is a standard procedure, however the generality of this method is impaired by a lack of specificity of the ultimate ring closure.

We report here a convenient preparation of pyrazolo[3,4-*b*]pyridines in synthetically useful yields by reaction of iminophosphoranes **10** and **11** with isocyanates and carbon dioxide. The iminophosphorane **9**, readily available from azidopyrazole **8** and triphenylphosphane[14], reacts with nitromethane in the presence of pyrrolidine to give crystalline iminophosphorane **10** in 55% yield. Compound **9** also reacts with acetone under the same reaction conditions to form the iminophosphorane **11** in 50% yield. However, when **9** is treated with an excess of nitromethane and pyrrolidine the iminophosphorane **12** is obtained in 73% yield. The $^1$H-NMR spectrum of **12** shows a singlet at $\delta$ = 2.17 due to the methyl group, the diastereotopic protons $CH(CH_2NO_2)_2$ attached at position 4 of the ring cause two double-doublets at $\delta$ = 4.34 and 4.53, and the methine group gives a multiplet at $\delta$ = 4.19. In the $^{13}$C-NMR spectrum the methyl, methylene, and methine carbons appear at $\delta$ = 13.84, 75.56, and 33.56, respectively, as was shown by 2D-NMR HCCOR and DEPT experiments.

To identify this compound unambiguously an X-ray structure determination was performed (Table 1, Fig. 1[15]). When comparing the pyrazole ring with the results of a search through the CSD system[15] (five determinations of just the pyrazole molecule with averages of N–N = 1.349, N–C = 1.330, C–C = 1.373 Å) it may be noticed that **12** has longer N–N and C–C distances and a shorter N–C bond length, mostly due to the elongation of N1–C5 (see




| 13 | R |
|---|---|
| a | $CH_3$ |
| b | $CH_2$=CH–$CH_2$ |
| c | $C_6H_5$ |
| d | 4-$CH_3C_6H_4$ |
| e | 4-$CH_3OC_6H_4$ |

| 15 | R |
|---|---|
| a | $CH_3$ |
| b | $C_6H_5$ |
| c | 4-$ClC_6H_5$ |
| d | 4-$CH_3C_6H_4$ |
| e | 4-$CH_3OC_6H_4$ |

Table 2). The angular values follow the pattern found in the CSD system, higher values at N1 and C3 and lower ones at the other atoms.

All substituents of the pyrazole ring turn out to be unsymmetrically, as far as the bond angles are concerned (see Table 2). The high thermal factors, describing the disorder affecting both substituents at C13, make the geometry of this moiety less reliable.

The C–N–$PPh_3$ substitution gives a geometry quite similar to that found in two iminophosphoranes[16,17] and in the (triphenylphosphonio)cyanoamide compound[18], with the peculiarity that the fragment opens the C–N–P angle and closes the N–P–Ph one that corresponds to a *trans* conformation of the two involved carbon atoms[19] (see Table 2).

The reaction of iminophosphorane **10** with aliphatic and aromatic isocyanates in dry toluene at reflux temperature

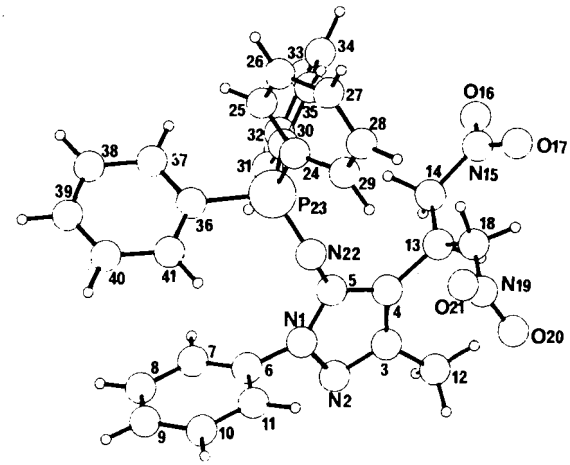



Figure 1. Molecular structure of compound **12** with the atomic numbers used in the crystallographic work

Table 1. Final atomic coordinates of **12**

| Atom | x/a | y/b | z/c |
|---|---|---|---|
| N1 | 0.6891( 3) | 0.0654( 3) | -0.0465( 4) |
| N2 | 0.6139( 4) | 0.0654( 3) | -0.1642( 4) |
| C3 | 0.6038( 4) | 0.1645( 4) | -0.1541( 4) |
| C4 | 0.6714( 4) | 0.2293( 3) | -0.0320( 4) |
| C5 | 0.7270( 4) | 0.1625( 3) | 0.0354( 4) |
| C6 | 0.7338( 4) | -0.0285( 3) | -0.0357( 4) |
| C7 | 0.6686( 5) | -0.1006( 4) | 0.0178( 6) |
| C8 | 0.7123( 6) | -0.1924( 5) | 0.0251( 8) |
| C9 | 0.8196( 6) | -0.2089( 5) | -0.0204( 8) |
| C10 | 0.8854( 7) | -0.1356( 6) | -0.0731( 9) |
| C11 | 0.8419( 5) | -0.0446( 5) | -0.0813( 7) |
| C12 | 0.5284( 6) | 0.1937( 5) | -0.2675( 6) |
| C13 | 0.6847( 5) | 0.3453( 4) | 0.0118( 7) |
| C14 | 0.5972( 8) | 0.3775( 5) | 0.1009(10) |
| N15 | 0.5852( 7) | 0.4857( 5) | 0.1466( 5) |
| O16 | 0.4970(16) | 0.5066(10) | 0.1877(16) |
| O17 | 0.6488(12) | 0.5489( 8) | 0.1337(27) |
| C18 | 0.7931(15) | 0.4031( 7) | 0.0061(21) |
| N19 | 0.8718( 7) | 0.3790( 7) | -0.0803( 9) |
| O20 | 0.8369(19) | 0.3722(19) | -0.1987(14) |
| O21 | 0.9587(11) | 0.3678(16) | -0.0330(29) |
| N22 | 0.8112( 3) | 0.1829( 3) | 0.1489( 4) |
| P23 | 0.8016( 1) | 0.1923( 1) | 0.3058( 1) |
| C24 | 0.9357( 3) | 0.2791( 3) | 0.3984( 4) |
| C25 | 0.9653( 4) | 0.2911( 4) | 0.5395( 5) |
| C26 | 1.0698( 5) | 0.3568( 4) | 0.6078( 5) |
| C27 | 1.1429( 5) | 0.4095( 4) | 0.5363( 6) |
| C28 | 1.1150( 5) | 0.3980( 5) | 0.3978( 7) |
| C29 | 1.0102( 4) | 0.3332( 4) | 0.3268( 5) |
| C30 | 0.6712( 4) | 0.2430( 3) | 0.3643( 4) |
| C31 | 0.5584( 4) | 0.1867( 3) | 0.3070( 5) |
| C32 | 0.4552( 4) | 0.2264( 4) | 0.3411( 6) |
| C33 | 0.4654( 5) | 0.3206( 4) | 0.4346( 6) |
| C34 | 0.5772( 5) | 0.3762( 4) | 0.4937( 6) |
| C35 | 0.6801( 4) | 0.3385( 3) | 0.4588( 5) |
| C36 | 0.8030( 3) | 0.0752( 3) | 0.3699( 4) |
| C37 | 0.7458( 5) | 0.0590( 4) | 0.4801( 6) |
| C38 | 0.7556( 6) | -0.0266( 5) | 0.5338( 7) |
| C39 | 0.8232( 6) | -0.0987( 4) | 0.4740( 7) |
| C40 | 0.8792( 7) | -0.0848( 5) | 0.3664( 7) |
| C41 | 0.8719( 5) | 0.0026( 4) | 0.3117( 5) |

Table 2. Selected geometrical parameters of **12** (Å, °)

| | | | |
|---|---|---|---|
| N1-N2 | 1.380(5) | C4-C13 | 1.497(7) |
| N2-C3 | 1.324(7) | C5-N22 | 1.359(5) |
| C3-C4 | 1.416(5) | C13-C14 | 1.450(12) |
| C4-C5 | 1.402(7) | C13-C18 | 1.372(16) |
| C5-N1 | 1.362(5) | C14-N15 | 1.447(10) |
| N1-C6 | 1.433(6) | N15-O16 | 1.167(20) |
| C3-C12 | 1.499(8) | N15-O17 | 1.070(16) |
| N22-P23 | 1.568(4) | C18-N19 | 1.330(21) |
| P23-C24 | 1.810(3) | N19-O20 | 1.191(17) |
| P23-C30 | 1.808(4) | N19-O21 | 1.090(19) |
| P23-C36 | 1.810(4) | | |
| C5-N1-C6 | 127.6(4) | N2-N1-C6 | 118.5(3) |
| N2-N1-C5 | 113.0(4) | N1-N2-C3 | 104.5(4) |
| N2-C3-C4 | 111.9(4) | C3-C4-C5 | 105.5(4) |
| C4-C5-N1 | 105.2(4) | N2-C3-C12 | 119.0(4) |
| C4-C3-C12 | 129.1(5) | C3-C4-C13 | 127.0(4) |
| C5-C4-C13 | 127.5(4) | C4-C5-N22 | 131.1(4) |
| N1-C5-N22 | 123.3(4) | C4-C13-C18 | 118.1(8) |
| C4-C13-C14 | 111.8(5) | C14-C13-C18 | 126.0(7) |
| C14-N15-O17 | 123.4(11) | C14-N15-O16 | 119.4(9) |
| O16-N15-O17 | 116.8(11) | C13-C18-N19 | 127.6(10) |
| C18-N19-O21 | 115.6(18) | C18-N19-O20 | 115.3(14) |
| O20-N19-O21 | 129.1(15) | C5-N22-P23 | 132.6(3) |
| N22-P23-C36 | 117.2(2) | N22-P23-C30 | 115.3(2) |
| N22-P23-C24 | 105.9(2) | C30-P23-C36 | 104.4(2) |
| C24-P23-C36 | 104.5(2) | C24-P23-C30 | 108.8(2) |
| N2-N1-C6-C7 | -88.1(5) | C3-C4-C13-C14 | 93.8(7) |
| C3-C4-C13-C18 | -107.8(10) | C4-C13-C18-N19 | 29.7(19) |
| C4-C13-C14-N15 | -174.4(7) | C13-C14-N15-O16 | 160.9(11) |
| C13-C14-N15-O17 | -11.5(17) | C13-C18-N19-O20 | 64.1(21) |
| C13-C18-N19-O21 | -115.5(19) | N1-C5-N22-P23 | -94.8(5) |
| C5-N22-P23-C24 | -152.7(4) | C5-N22-P23-C30 | -32.4(5) |
| C5-N22-P23-C36 | 91.3(5) | N22-P23-C36-C37 | -151.2(4) |
| N22-P23-C30-C31 | 62.1(4) | N22-P23-C24-C25 | -169.5(4) |

leads directly to the corresponding 6-[alkyl(aryl)amino]-3-methyl-5-nitro-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridines **13** in moderate to good yields. Presumably the convertion **10** → **13** involves initial aza Wittig reaction between the iminophosphorane and the isocyanate to give a carbodiimide as highly reactive intermediate which easily undergoes electrocyclic ring closure to give the fused pyridine. Iminophosphorane **10** also reacts with carbon dioxide at 130°C in a sealed glass tube to give the pyrazolo[3,4-*b*]pyridine **14**. Similarly, iminophosphorane **11** reacts with isocyanates and carbon dioxide to give the pyrazolo[3,4-*b*]pyridines **15** and **16**, respectively.

The methodology described in this paper affords a new and general route to fused pyridines with variable substituents at the pyridine ring. These structurs (e.g. nitropyridines), which would be difficult to prepare by classical synthetic routes, are formed in a simple one-pot procedure from readily available starting materials.

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## Experimental

Microanalyses: Perkin-Elmer 240C instrument. – $^1$H- and $^{13}$C-NMR spectra: Varian FT-80 or Varian XL-300 instruments. – IR spectra: Nicolet 5DX, Nujol used in all cases. – Mass spectra: Hewlett-Packard 5993-C. – Melting points (uncorrected): Kofler hot-stage apparatus.

*X-Ray Crystallography of* **12**: $C_{31}H_{28}N_5O_4P$, $M$ = 565.57, triclinic, space group $P\bar{1}$, $a$ = 11.3306(6), $b$ = 13.3281(6), $c$ = 10.0237(5) Å, $\alpha$ = 102.239(4), $\beta$ = 96.057(3), $\gamma$ = 97.829(4)°, $D_c$ = 1.294 g cm$^{-3}$, $Z$ = 2. Cell obtained from a least-squares fit using 91 reflexions up to $\Theta$ = 45° and Cu-$K_\alpha$ radiation. A transparent yellow prism-like sample (0.50 × 0.23 × 0.23 mm) was used for the analysis on a Philips PW 1100 diffractometer, with Cu-$K_\alpha$ radiation, graphite monochromator, $\omega/2\Theta$ scans, bisecting geometry, 1 × 1° detector apertures, 1.6° scan width and spending 1 min per reflexion. Good stability for the sample checked every 90 min.

A $3\sigma(I)$ criterion gave 4112 observed reflexions, up to 65° in $\Theta$. No absorption correction was applied, $\mu$ = 11.86 cm$^{-1}$. The structure was solved by direct methods[20] and refined by full matrix least-squares procedures. All the hydrogen atoms (except those of the C14 and C18 atoms) were located on a difference synthesis. The $NO_2$ groups present the higest thermal values, and some unsuccessful disorder models have been tried out. An empirical weighting scheme as to give no trends in $\langle\omega\Delta^2F\rangle$ vs. $\langle|F_o|\rangle$ and $\langle(\sin\Theta)/\lambda\rangle$ was introduced. The maximum peak in the final $\Delta F$ was of 0.62$e$Å$^{-3}$. The final $R$ and $R_w$ values were 0.090 and 0.111, respectively. Most of the calculations were performed with the XRAY 76 system[21] on a VAX 11/750 computer. The atomic scattering factors were taken from the International Tables[22].

*Ethyl 5-Phenyl-2-[(triphenylphosphoranyliden)amino]-2,4-pentadienoate* (**3**): A solution of triphenylphosphane (1.31 g, 5.0 mmol) in dry dichloromethane (20 ml) was added dropwise under nitrogen at 0°C to a solution of ethyl 2-azido-5-phenyl-2,4-pentadienoate (**2**)[12] (1.21 g, 5.0 mmol) in dry dichloromethane (10 ml). The reaction mixture was stirred at room temp. for 24 h. Then the solution was concentrated to dryness, and the residual material was crystallized from benzene/ether (1:1, v/v) to give **3** as yellow prisms: 1.67 g (77%), m.p. 111–113°C. – IR: 1693 cm$^{-1}$, 1557, 1234, 1217. – $^1$H NMR ($CDCl_3$): δ = 1.1 (t, 3H), 3.95 (q, 2H), 6.6 (m, 1H), 6.9 (m, 1H), 7.1–8.1 (m, 21H). – MS (70 eV): *m/z* (%) = 477 ($M^+$, 5), 262 (100), 183 (41), 108 (48).

$C_{31}H_{28}NO_2P$ (477.5) Calcd. C 77.96 H 5.90 N 2.93
Found C 77.52 H 5.81 N 2.76

*Ethyl 6-[Alkyl(aryl)amino]-5-phenyl-2-pyridinecarboxylates* **5**. – *General Procedure:* To a solution of **3** (0.48 g, 1.0 mmol) in dry toluene (20 ml) the appropriate isocyanate (1.0 mmol) in dry toluene (10 ml) was added dropwise under nitrogen at room temp. The resultant solution was refluxed for 12 h. After cooling, the solution was concentrated to dryness, and the residual material was purified by column chromatography (silica gel and dichloromethane/hexane 7:3 as eluent) followed by crystallization from dichloromethane/hexane to give **5**.

*Ethyl 6-[Ethylamino]-5-phenyl-2-pyridinecarboxylate* (**5a**): Yield 79%, oil. – IR: 3437 cm$^{-1}$, 1710, 1572, 1217, 764. – $^1$H NMR ($CDCl_3$): δ = 1.2 (t, 3H), 1.4 (t, 3H), 4.05 (m, 2H), 4.5 (q, 2H), 7.6 (m, 7H). – MS (70 eV): *m/z* (%) = 270 ($M^+$, 60), 241 (33), 195 (100), 168 (33), 153 (39), 140 (39), 115 (38).

$C_{16}H_{18}N_2O_2$ (270.3) Calcd. C 71.17 H 6.66 N 10.37
Found C 71.06 H 6.87 N 10.49

*Ethyl 5-Phenyl-6-(phenylamino)-2-pyridinecarboxylate* (**5b**): Yield 68%, m.p. 101–103 C, colorless prisms. – IR: 3420 cm$^{-1}$, 1716, 1524, 1265, 748, 690. – $^1$H NMR ($CDCl_3$): δ = 1.45 (t, 3H), 4.5 (q, 2H), 7.6 (m, 13H). – MS (70 eV): *m/z* (%) = 318 ($M^+$, 61), 244 (53), 243 (100), 140 (60), 115 (53), 77 (61).

$C_{20}H_{18}N_2O_2$ (318.4) Calcd. C 75.45 H 5.69 N 8.79
Found C 75.32 H 5.43 N 8.86

*Ethyl 6-(4-Bromophenylamino)-5-phenyl-2-pyridinecarboxylate* (**5c**): Yield 71%, m.p. 92–92°C, yellow prisms. – IR: 3415 cm$^{-1}$, 1721, 1523, 1257, 1143, 758. – $^1$H NMR ($CDCl_3$): δ = 1.5 (t, 3H),

4.6 (q, 2H), 6.9 (s, broad, 1H), 7.6 (m, 11H). – MS (70 eV): *m/z* (%) = 397 ($M^+$ + 2, 55), 395 ($M^+$, 57), 243 (100), 140 (62), 115 (60).

$C_{20}H_{17}BrN_2O_2$ (397.3) Calcd. C 60.46 H 4.31 N 7.05
Found C 60.39 H 4.27 N 7.12

*Ethyl 6-(4-Chlorophenylamino)-5-phenyl-2-pyridinecarboxylate* (**5d**): Yield 71%, m.p. 75–77°C, yellow prisms. – IR: 3420 $cm^{-1}$, 1721, 1599, 1518, 1104, 713. – $^1H$ NMR ($CDCl_3$): δ = 1.5 (t, 3H), 4.43 (q, 2H), 6.8 (s, broad, 1H), 7.6 (m, 11H). – MS (70 eV): *m/z* (%) = 354 ($M^+$ + 2, 30), 352 ($M^+$, 100), 305 (53), 278 (36), 243 (62), 147 (58), 115 (56).

$C_{20}H_{17}ClN_2O_2$ (352.8) Calcd. C 68.08 H 4.85 N 7.93
Found C 68.12 H 4.83 N 7.86

*Ethyl 6-(4-Methylphenylamino)-5-phenyl-2-pyridinecarboxylate* (**5e**): Yield 86%, m.p. 96–98°C, colorless prisms. – IR: 3420 $cm^{-1}$, 1716, 1517, 1263, 1143, 810, 758, 701. – $^1H$ NMR ($CDCl_3$): δ = 1.55 (t, 3H), 2.3 (t, 3H), 4.5 (q, 2H), 6.8 (s, broad, 1H), 7.6 (m, 11H). – MS (70 eV): *m/z* (%) = 332 ($M^+$, 85), 303 (20), 285 (33), 258 (57), 242 (30), 140 (66), 115 (68), 69 (100).

$C_{21}H_{20}N_2O_2$ (332.4) Calcd. C 75.88 H 6.06 N 8.42
Found C 75.90 H 6.01 N 8.38

*Ethyl 6-(4-Methoxyphenylamino)-5-phenyl-2-pyridinecarboxylate* (**5f**): Yield 72%, m.p. 66–67°C, colorless prisms. – IR: 3426 $cm^{-1}$, 1715, 1656, 1241, 1159, 764, 706. – $^1H$ NMR ($CDCl_3$): δ = 1.55 (t, 3H), 4.03 (s, 3H), 4.72 (q, 2H), 6.8 (s, broad, 1H), 7.1–7.9 (m, 11H). – MS (70 eV): *m/z* (%) = 348 ($M^+$, 100), 319 (22), 242 (50), 140 (37), 115 (63).

$C_{21}H_{20}N_2O_3$ (348.4) Calcd. C 72.39 H 5.78 N 8.04
Found C 72.27 H 5.83 N 7.93

*Isolation and Thermal Cyclization of the Carbodiimide* **4** (R = *tert*-Butyl): A solution of *tert*-butyl isocyanate (0.11 g, 1.67 mmol) in dry toluene (20 ml) was added dropwise under nitrogen at room temp. to a solution of **3** (0.80 g, 1.67 mmol) in dry toluene (20 ml). The reaction mixture was stirred at reflux temp. for 24 h. After cooling, the solution was concentrated to dryness, and the residual material was purified by column chromatography (silica gel, ethyl acetate/hexane 3:7 as eluent) to give **4** (R = *t*Bu) as oil: 0.36 g (72%). – IR: 2135 $cm^{-1}$, 1715, 1234, 723, 696. – $^1H$ NMR ($CDCl_3$): δ = 1.4 (t, 3H), 1.45 (s, 9H), 4.45 (q, 2H), 6.8 (d, 1H), 7.05 (d, 1H), 7.1–7.7 (m, 6H).

Compound **4** (0.36 g, 1.2 mmol) was heated under nitrogen at 160–170°C for 2 h to give *ethyl 6-(tert-butylamino)-5-phenyl-2-pyridinecarboxylate:* 0.24 g (69%) as oil. – IR: 3437 $cm^{-1}$, 1719, 1508, 1254, 1140, 765. – $^1H$ NMR ($CDCl_3$): δ = 1.43 (t, 3H), 1.5 (s, 9H), 4.5 (q, 2H), 7.56 (m, 8H). – MS (70 eV): *m/z* (%) = 298 ($M^+$, 5), 242 (23), 241 (30), 77 (25), 69 (84), 41 (100).

$C_{18}H_{22}N_2O_2$ (298.4) Calcd. C 72.45 H 7.43 N 9.38
Found C 72.30 H 7.69 N 9.55

*Isothiocyanate* **6**: Carbon disulfide (0.23 g, 3.0 mmol) was added dropwise under nitrogen at room temp. to a solution of **3** (0.48 g, 1.0 mmol) in dry toluene (20 ml). The resultant mixture was stirred at reflux temp. for 12 h. After cooling, the solvent was removed, and the residual material was recrystallized from toluene/hexane (1:1, v/v) to give **6** as colorless prisms: 0.20 g (73%), m.p. 82–84°C. – IR: 2050 $cm^{-1}$, 1715, 1280, 1245, 1030, 747. – $^1H$ NMR ($CDCl_3$): δ = 1.4 (t, 3H), 4.35 (q, 2H), 7.3–7.8 (m, 8H). – MS (70 eV): *m/z* (%) = 259 ($M^+$, 20), 185 (25), 128 (20), 115 (15), 95 (23), 69 (100). $C_{14}H_{13}NO_2S$ (259.5) Calcd. C 64.48 H 5.05 N 5.40
Found C 64.39 H 5.12 N 5.32

*Iminophosphoranes* **10** *and* **11**. – *General Procedure:* To a solution of 3-methyl-1-phenyl-5-[(triphenylphosphoranylidene)amino]-1*H*-pyrazole-4-carboxaldehyde (**9**)[14] (1.0 g, 2.17 mmol) in anhydrous ethanol (20 ml) the appropriate activated methylene compound (nitromethane or acetone) (2.17 mmol) and pyrrolidine (0.31 g, 4.34 mmol) were added. The resultant mixture was stirred under nitrogen at 40°C for 4 h. The separated solid was collected by filtration, washed with ether, air-dried, and recrystallized from ethanol.

*3-Methyl-4-(2-nitrovinyl)-1-phenyl-5-[(triphenylphosphoranyliden)amino]-1H-pyrazole* (**10**): Yield 55%, m.p. 180–181°C, yellow prisms. – IR: 1608 $cm^{-1}$, 1528, 1296, 1269, 1177, 1109. – $^1H$ NMR ($CDCl_3$): δ = 2.26 (s, 3H), 6.97–7.66 (m, 22H). – MS (70 eV): *m/z* (%) = 504 ($M^+$, 5), 304 (20), 262 (26), 183 (100), 108 (49).

$C_{30}H_{25}N_4PO_2$ (504.5) Calcd. C 71.42 H 4.99 N 11.10
Found C 71.60 H 4.80 N 11.23

*3-Methyl-4-(3-oxo-1-butenyl)-1-phenyl-5-[(triphenylphosphoranyliden)amino]-1H-pyrazole* (**11**): Yield 50%, m.p. 199–200°C, orange prisms. – IR: 1676 $cm^{-1}$, 1579, 1528, 1109, 764, 718, 690. – $^1H$ NMR ($CDCl_3$): δ = 1.78 (s, 3H), 2.43 (s, 3H), 6.26 (d, 1H, *J* = 17 Hz), 7.2–7.9 (m, 21H). – MS (70 eV): *m/z* (%) = 501 ($M^+$, 22), 458 (10), 262 (28), 183 (100), 77 (56).

$C_{32}H_{28}N_3OP$ (501.6) Calcd. C 76.63 H 5.63 N 8.38
Found C 76.80 H 5.49 N 8.42

*Iminophosphorane* **12**: To a solution of **9** (1.0 g, 2.17 mmol) in anhydrous ethanol (20 ml) nitromethane (0.39 g, 6.5 mmol) and pyrrolidine (0.46 g, 6.5 mmol) were added. The resultant mixture was stirred under nitrogen at 40°C for 4 h. The separated solid was collected by filtration, washed with ether, air-dried, and recrystallized from ethanol to give **12** as yellow prisms: 0.89 g (73%), m.p. 191–192°C. – IR: 1557 $cm^{-1}$, 1438, 1381, 1115, 718, 696. – $^1H$ NMR ($CDCl_3$): δ = 2.17 (s, 3H, $CH_3$), 4.19 (q, 1H), 4.34 (dd, 2H, $-CH_2-$, *J* = 8/13 Hz), 4.53 (dd, 2H, *J* = 8/13 Hz), 7.02–7.09 (m, 5H), 7.31–7.42 (m, 12H), 7.46–7.53 (m, 3H). – $^{13}C$ NMR ($CDCl_3$): δ = 13.8 ($CH_3$), 33.5 (CH), 75.6 ($CH_2$), 126.1, 126.6, 128.7, 128.8, 129.0, 132.2, 132.3, 132.5, 139.9, 149.5. – MS (70 eV): *m/z* (%) = 565 ($M^+$, 5), 278 (35), 277 (91), 262 (30), 184 (20), 183 (100), 108 (27), 77 (87).

$C_{31}H_{28}N_5O_4P$ (565.5) Calcd. C 65.84 H 4.99 N 12.38
Found C 65.62 H 5.11 N 12.49

*5-Substituted 6-[Alkyl(aryl)amino]-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridines* **13** *and* **15**. – *General Procedure:* To a solution of the iminophosphorane **10** or **11** (5.0 mmol) in dry toluene (10 ml), a solution of the appropriate isocyanate (5.0 mmol) in dry toluene (5 ml) was added dropwise under nitrogen at room temp. The reaction mixture was refluxed for 5 h. After cooling, the solvent was removed, and the residual material was slurried with cold ethanol (20 ml). The precipitated solid was separated by filtration, air-dried, and recrystallized from ethanol.

*6-(Methylamino)-3-methyl-5-nitro-1-phenyl-1H-pyrazolo[3,4-b]pyridine* (**13a**): Yield 60%, m.p. 121–122°C, yellow prisms. – IR: 3398 $cm^{-1}$, 1630, 1596, 1438, 1376, 1115, 752. – $^1H$ NMR ($CDCl_3$): δ = 2.58 (s, 3H), 3.23 (d, 3H, *J* = 5 Hz, $CH_3NH$), 7.26–7.76 (m, 3H), 8.16–8.56 (m, 2H), 8.90 (s, broad, 1H, NH). – MS (70 eV): *m/z* (%) = 283 ($M^+$, 100), 266 (44), 209 (50), 167 (14), 77 (61).

$C_{14}H_{13}N_5O_2$ (283.3) Calcd. C 59.36 H 4.63 N 24.73
Found C 59.28 H 4.40 N 24.83

*6-(Allylamino)-3-methyl-5-nitro-1-phenyl-1H-pyrazolo[3,4-b]pyridine* (**13b**): Yield 50%, m.p. 127–128°C, yellow prisms. – IR: 3398 $cm^{-1}$, 1625, 1597, 1438, 1381, 1296, 1104, 752. – $^1H$ NMR ($CDCl_3$): δ = 2.51 (s, 3H), 4.2–4.5 (m, 2H), 5.2–5.6 (m, 2H), 5.9–6.5 (m, 2H), 7.43–8.83 (m, 6H), 9.0 (s, broad, 1H, NH). –

MS (70 eV): *m/z* (%) = 309 ($M^+$, 24), 308 (23), 294 (100), 292 (26), 262 (29), 261 (76), 77 (38).

$C_{16}H_{15}N_5O_2$ (309.3) Calcd. C 62.13 H 4.89 N 22.64
Found C 62.01 H 4.72 N 22.90

*3-Methyl-5-nitro-1-phenyl-6-(phenylamino)-1H-pyrazolo[3,4-b]-pyridine* (**13c**): Yield 55%, m.p. 143–144 °C, red prisms. – IR: 3347 $cm^{-1}$, 1580, 1331, 1280, 1180, 753. – $^1H$ NMR ([$D_6$]DMSO): δ = 2.50 (s, 3H), 6.80–8.77 (m, 10H), 9.10 (s, 1H), 10.36 (s, broad, 1H, NH). – MS (70 eV): *m/z* (%) = 345 ($M^+$, 100), 344 (20), 299 (15), 222 (6), 156 (10), 77 (63).

$C_{19}H_{15}N_5O_2$ (345.3) Calcd. C 66.08 H 4.38 N 20.28
Found C 66.19 H 4.17 N 20.32

*3-Methyl-6-(4-methylphenylamino)-5-nitro-1-phenyl-1H-pyrazolo[3,4-b]pyridine* (**13d**): Yield 56%, m.p. 154–155 °C, red prisms. – IR: 3330 $cm^{-1}$, 1602, 1517, 1393, 1279, 1138, 764. – $^1H$ NMR ($CDCl_3$): δ = 2.46 (s, 3H), 2.56 (s, 3H), 6.66 (d, 1H, *J* = 8 Hz), 7.1–8.5 (m, 7H), 9.0 (d, 1H, *J* = 8 Hz), 9.23 (s, 1H), 10.46 (s, broad, 1H, NH). – MS (70 eV): *m/z* (%) = 359 ($M^+$, 86), 358 (10), 313 (100), 311 (12), 207 (10), 156 (15), 91 (10), 77 (59).

$C_{20}H_{17}N_5O_2$ (359.4) Calcd. C 66.65 H 5.03 N 19.43
Found C 66.42 H 4.93 N 19.28

*6-(4-Methoxyphenylamino)-3-methyl-5-nitro-1-phenyl-1H-pyrazolo[3,4-b]pyridine* (**13e**): Yield 60%, m.p. 163–163 °C, red prisms. – IR: 3320 $cm^{-1}$, 1602, 1574, 1506, 1274, 1228, 1132, 1030, 788. – $^1H$ NMR ($CDCl_3$): δ = 2.66 (s, 3H), 3.86 (s, 3H), 6.7–8.5 (m, 9H), 10.40 (s, broad, 1H, NH). – MS (70 eV): *m/z* (%) = 375 ($M^+$, 69), 360 (16), 329 (52), 313 (16), 285 (15), 103 (21), 77 (100).

$C_{20}H_{17}N_5O_3$ (375.4) Calcd. C 63.82 H 4.82 N 18.61
Found C 63.60 H 5.00 N 18.85

*5-Acetyl-3-methyl-6-(methylamino)-1-phenyl-1H-pyrazolo[3,4-b]pyridine* (**15a**): Yield 43%, m.p. 119–120 °C, yellow prisms. – IR: 3313 $cm^{-1}$, 1659, 1625, 1596, 1268. – $^1H$ NMR ($CDCl_3$): δ = 2.53 (s, 3H, $CH_3CO$), 2.58 (s, 3H, $CH_3$), 3.15 (d, 3H, *J* = 5 Hz, $CH_3NH$), 7.26–7.86 (m, 3H), 8.30 (s, 1H), 8.40–8.66 (m, 2H), 9.33 (s, broad, 1H, NH). – MS (70 eV): *m/z* (%) = 280 ($M^+$, 36), 279 (10), 265 (30), 237 (43), 77 (100).

$C_{16}H_{16}N_4O$ (280.3) Calcd. C 68.55 H 5.75 N 19.98
Found C 68.72 H 5.60 N 20.03

*5-Acetyl-3-methyl-1-phenyl-6-(phenylamino)-1H-pyrazolo[3,4-b]pyridine* (**15b**): Yield 64%, m.p. 154–155 °C, yellow prisms. – IR: 3392 $cm^{-1}$, 1647, 1597, 1534, 1234, 752. – $^1H$ NMR ($CDCl_3$): δ = 2.47 (s, 3H, $CH_3CO$), 2.58 (s, 3H, $CH_3$), 7.06–8.06 (m, 8H), 8.17–8.50 (m, 3H), 11.63 (s, broad, 1H, NH). – MS (70 eV): *m/z* (%) = 342 ($M^+$, 33), 341 (15), 327 (10), 299 (8), 251 (21), 77 (100).

$C_{21}H_{18}N_4O$ (342.4) Calcd. C 73.67 H 5.30 N 16.36
Found C 73.89 H 5.12 N 16.48

*5-Acetyl-6-(4-chlorophenylamino)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridine* (**15c**): Yield 55%, m.p. 184–185 °C, yellow prisms. – IR: 3109 $cm^{-1}$, 1647, 1613, 1585, 1234, 1087. – $^1H$ NMR ($CDCl_3$): δ = 2.46 (s, 3H, $CH_3CO$), 2.56 (s, 3H, $CH_3$), 7.16–7.93 (m, 7H), 8.06–8.50 (m, 3H), 11.60 (s, broad, 1H, NH). – MS (70 eV): *m/z* (%) = 378 ($M^+$ + 2, 33), 377 ($M^+$ + 1, 33), 376 ($M^+$, 100), 361 (15), 252 (17), 251 (97), 111 (18), 77 (71).

$C_{21}H_{17}ClN_4O$ (376.8) Calcd. C 66.93 H 4.55 N 14.87
Found C 67.17 H 4.32 N 14.93

*5-Acetyl-3-methyl-6-(4-methylphenylamino)-1-phenyl-1H-pyrazolo[3,4-b]pyridine* (**15d**): Yield 79%, m.p. 166–167 °C, yellow prisms. – IR: 3301 $cm^{-1}$, 1647, 1602, 1183, 1121, 752. – $^1H$ NMR ($CDCl_3$): δ = 2.32 (s, 3H, $CH_3C_6H_4$), 2.38 (s, 3H, $CH_3CO$), 2.48 (s, 3H, $CH_3$), 6.96 (d, 2H, *J* = 9 Hz), 7.15–7.32 (m, 3H), 7.5 (d, 2H, *J* = 9 Hz), 7.87–8.20 (m, 3H), 11.2 (s, broad, 1H, NH). – MS (70 eV): *m/z* (%) = 356 ($M^+$, 41), 341 (15), 313 (15), 251 (32), 91 (24), 77 (100),

$C_{22}H_{20}N_4O$ (356.4) Calcd. C 74.14 H 5.66 N 15.72
Found C 74.26 H 5.48 N 15.87

*5-Acetyl-6-(4-methoxyphenylamino)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridine* (**15e**): Yield 70%, m.p. 138–139 °C, yellow prisms. – IR: 3352 $cm^{-1}$, 1647, 1608, 1551, 1262, 1234, 1036, 775. – $^1H$ NMR ($CDCl_3$): δ = 2.5 (s, 3H, $CH_3CO$), 2.6 (s, 3H, $CH_3$), 3.9 (s, 3H, $CH_3O$), 7.06 (d, 2H, *J* = 9 Hz), 7.33–7.70 (m, 3H), 7.86 (d, 2H, *J* = 9 Hz), 8.20–8.56 (m, 3H), 11.4 (s, broad, 1H, NH). – MS (70 eV): *m/z* (%) = 372 ($M^+$, 41), 357 (24), 329 (10), 251 (21), 91 (10), 77 (100).

$C_{22}H_{20}N_4O_2$ (372.4) Calcd. C 71.00 H 5.41 N 15.04
Found C 71.25 H 5.23 N 15.18

*5-Substituted 1,7-Dihydro-3-methyl-1-phenyl-6H-pyrazolo[3,4-b]-pyridin-6-ones* **14** *and* **16**. – *General Procedure:* Iminophosphorane **10** or **11** (1.0 mmol), dry toluene (20 ml), and excess of solid carbon dioxide were heated in a sealed tube at 130 °C for 15 h. After cooling, the solvent was removed under reduced pressure, and the crude product was slurried with ether (20 ml), filtered, and recrystallized from the appropriate solvent.

*1,7-Dihydro-3-methyl-5-nitro-1-phenyl-6H-pyrazolo[3,4-b]pyridin-6-one* (**14**): Yield 52%, m.p. 242–244 °C, yellow prisms from methanol. – IR: 3301 $cm^{-1}$, 1630, 1506, 1325, 1302, 758. – $^1H$ NMR ($CDCl_3$): δ = 2.63 (s, 3H, $CH_3$), 7.3–7.7 (m, 5H), 8.05 (s, 1H, 4-H), 9.1 (s, 1H, NH). – MS (70 eV): *m/z* (%) = 270 ($M^+$, 5), 256 (16), 213 (15), 149 (10), 129 (14), 121 (12), 69 (100).

$C_{13}H_{10}N_4O_3$ (270.2) Calcd. C 57.75 H 3.73 N 20.73
Found C 57.60 H 3.90 N 20.53

*5-Acetyl-1,7-dihydro-3-methyl-1-phenyl-6H-pyrazolo[3,4-b]pyridin-6-one* (**16**): Yield 57%, m.p. 183–184 °C, colorless prisms from chloroform. – IR: 3359 $cm^{-1}$, 1648, 1625, 1596, 1250, 764. – $^1H$ NMR ($CDCl_3$): δ = 2.6 (s, 3H, $CH_3CO$), 2.72 (s, 3H, $CH_3$), 7.25–7.80 (m, 3H), 8.2–8.6 (m, 3H), 13.5 (s, broad, 1H, NH). – MS (70 eV): *m/z* (%) = 267 ($M^+$, 72), 253 (20), 252 (100), 128 (20), 91 (12), 77 (57).

$C_{15}H_{13}N_3O_2$ (267.3) Calcd. C 67.40 H 4.90 N 15.72
Found C 67.56 H 4.79 N 15.87

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[1] A preliminary communication of a part of this work has appeared: P. Molina, P. M. Fresneda, P. Alarcón, *Tetrahedron Lett.* **29** (1988) 379.

[2] A. Dondoni, *Heterocycles* **14** (1980) 1947; D. L. Boger, *Tetrahedron* **39** (1983) 2869.

[3] J. C. Jutz, *Top. Curr. Chem.* **73** (1978) 125.

[4] P. Molina, P. M. Fresneda, F. Hurtado, *Synthesis* **1987**, 45; P. Molina, P. M. Fresneda, *J. Chem. Soc., Perkin Trans. 1*, **1988**, 1819.

[5] T. Saito, M. Natane, M. Endo, M. Yamashita, Y. Oyameda, S. Motoki, *Chem. Lett.* **1986**, 135.

[6] F. Eloy, A. Deryckere, *Helv. Chim. Acta* **52** (1969) 1755.

[7] A. E. Baydar, G. H. Boyd, *J. Chem. Soc., Chem. Commun.* **1976**, 718.
[8] R. A. Abramovitch, G. N. Knaus, *J. Chem. Soc., Chem. Commun.* **1974**, 238; T. L. Gilchrist, C. J. Harris, C. W. Rees, *ibid.* **1974**, 487; R. Breslow, M. Oda, J. Pecoraro, *Tetrahedron Lett.* **1972**, 4415.
[9] P. Molina, *Bull. Soc. Chim. Belg.* **95** (1986) 973, and references cited therein.
[10] F. Eloy, A. Deryckere, *J. Heterocycl. Chem.* **7** (1970) 1191.
[11] L. E. Overman, S. Tsuboi, *J. Am. Chem. Soc.* **99** (1977) 2813; L. E. Overman, S. Tsuboi, J. P. Roos, G. F. Taylor, *ibid.* **102** (1980) 747.
[12] J. P. Bonkon-Poba, M. Farnier, R. Guilar, *Tetrahedron Lett.* **1979**, 1717.
[13] C. R. Hardy, *Adv. Heterocycl. Chem.* **36** (1984) 343.
[14] P.Molina, A. Arques, M. V. Vinader, J. Becher, K. Brodum, *J. Org. Chem.*, in press.
[15] F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. J. Hummelink-Peters, O. Kennards, W. D. S. Northerwell, J. R. Rogers, D. G. Watson, *Acta Cryst., Sect. B*, **35** (1979) 2331.
[16] J. E. Hewlins, *J. Chem. Soc. B*, **1971**, 942.
[17] P. J. Butterfield, J. C. Tebby, T. J. King, *J. Chem. Soc., Perkin Trans 1*, **1978**, 1237.
[18] J. Kaiser, H. Hartung, R. Richter, *Z. Anorg. Allg. Chem.* **469** (1980) 188.
[19] Further details of the crystal structure investigation are available on request from Fachtinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depositary number CSD-53317, the names of the author, and the journal citation.
[20] P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declerc, M. M. Woolfson, *Multan 80 System* (1980), University of York, England.
[21] J. M. Stewart, P. A. Machin, C. W. Dickinson, M. L. Ammon, H. Heck, H. Flack, *The X-ray System* (1976), Technical report TR-446, Computer Science Center, University of Maryland, USA.
[22] *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, England, 1974.

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