

Dichloro(diisopropylamino)phosphonio-[5(4*H*)oxopyrazol-4-ylide-5-one]: Synthesis and Properties

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ABSTRACT: Chlorination of the 4-[chloro-(diisopropylamino)phosphino]pyrazole **1** leads to the dichlorophosphonium chloride **2**, which immediately after its formation transforms into the dichloro(diisopropylamino)phosphonio[5(4)oxopyrazol-4-ylide-5-one] **3**, as a result of dealkylation through loss of ethyl chloride. Reactions of **3** with various nucleophilic reagents were studied. The partial hydrolysis of **3** in the presence of nitriles, resulting in new phosphorus-containing cyclic systems, is of particular interest. It was demonstrated that chlorination of the *P*-dichloropyrazolylphosphine **A** leads to the stable tetrachlorophosphorane **12**. The C–P bond of **12** is broken upon heating. An X-ray structure determination of compound **11b** revealed a planar central heterocycle (mean deviation 0.029 Å). © 2003 Wiley Periodicals, Inc. *Heteroatom Chem* 14:452–458, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10177

INTRODUCTION

One of the most important types of *P*-heterosubstituted phosphorus ylides studied intensively in recent years are ylides containing a halogen atom at phosphorus, otherwise called *P*-halogenoylides. Ready availability, convenient methods of synthesis, and ability to take part in various reactions account for the great interest in *P*-halogenoylides, and provide extensive experimental data on phosphorus *P*-monohalogenoylide chemistry [1]. At the same time, the chemistry of *P,P*-dihalogenoylides remains a comparatively poorly investigated area of organophosphorus chemistry because the compounds are not easily accessible. Thus, only one *P,P*-dichloroylide is known [2].

RESULTS AND DISCUSSION

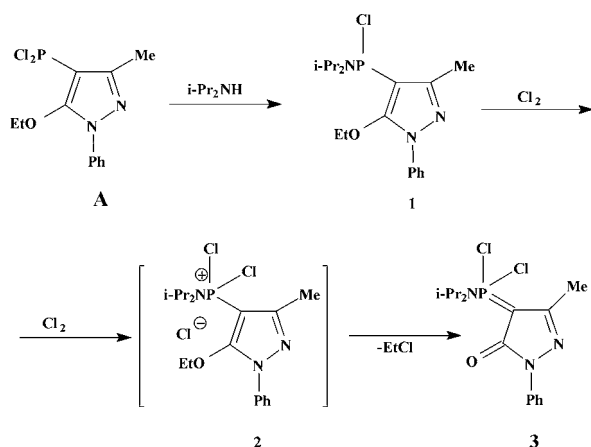
Previously we described the transformation of 4-phosphorylated-5-alkoxy-pyrazoles into ylides [3] including monohalogenoylides [4], which are now used for the synthesis of dichloroylides. It was shown that chlorination of the pyrazole-substituted diisopropylaminochlorophosphine **1** (via the dichlorophosphonium chloride **2**) leads to the formation of the dichloroylide **3**.

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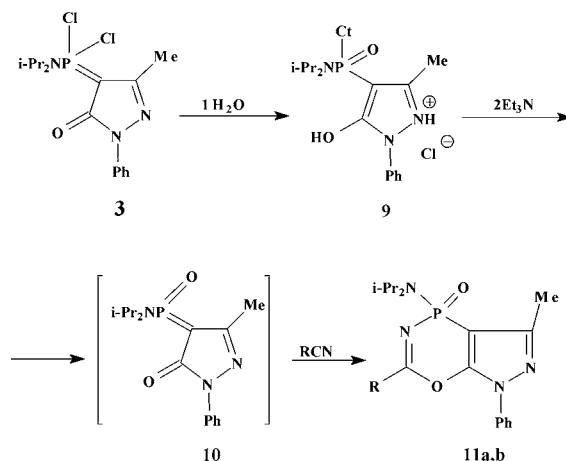
Dealkylation of compound **2** takes place as soon as it is formed; it cannot be detected by ^{31}P NMR spectroscopy.



The dichloroylide **3** is a thermally stable slightly colored substance, which is crystallized from heptane. The absence of a 1,2(P $\rightarrow$ C) chloro shift to the α -chlorophosphine in the case of compound **3** can be explained by the stabilizing effect of the pyrazolone ring, reducing the negative charge at the ylidic phosphorus atom. The structure of **3** was confirmed by ^{31}P , ^1H , and ^{13}C NMR spectroscopy (see Tables 1–3) and elemental analysis. The $\delta(^{13}\text{C})$ value of the P=C carbon atom lies in the neighborhood of 76 ppm, and the signal is a doublet with a J_{CP} coupling constant of 188 Hz. The ylide structure of compound **3** was also confirmed by IR-spectroscopy: the IR absorption band corresponding to the carbonyl group (1636 cm^{-1} in a KBr pellet/ 1628 cm^{-1} in CDCl_3 solution), and the absorption band corresponding to the P=C group at 1230 cm^{-1} were observed.

The chlorine atoms in the dichloroylide **3** at the positively charged, electrophilic phosphorus atom

can readily be substituted by various groups through interaction with O-, N-, and S-nucleophiles, giving compounds **5–8**. The chlorine atoms can also easily be substituted with the bulky *tert*-butylamino groups with formation of compound **7b**.



a: R = Me, b: R = Ph

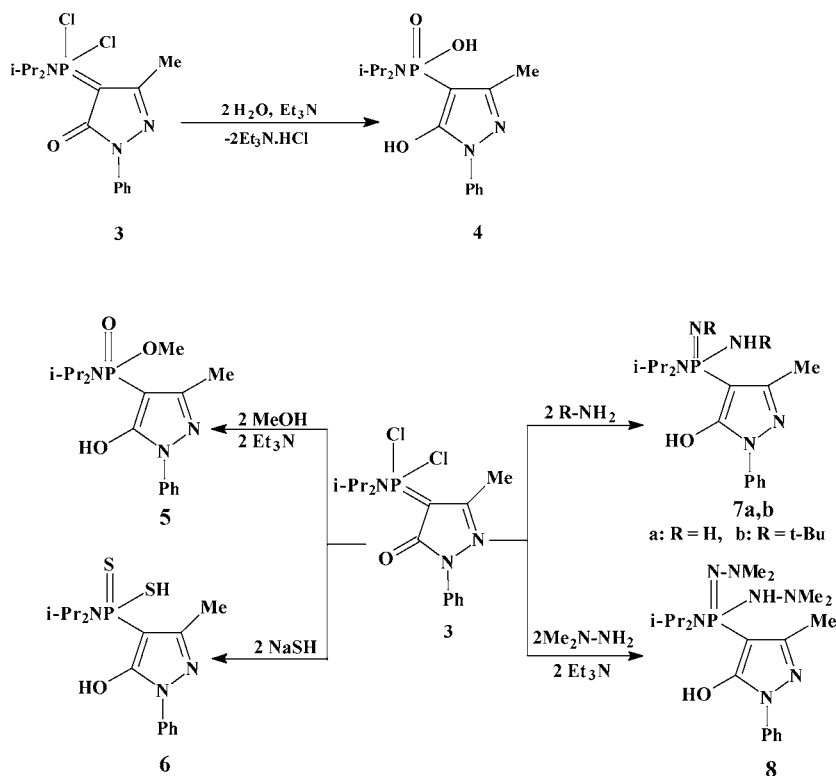
These reactions are facile; they proceed in high yields and open up broad opportunities for the synthesis of compounds involving essentially any substituents at the phosphorus atom.

The partial hydrolysis of the dichloroylide **3**, resulting in the formation of the hydrochloride of the amidochlorophosphonate **9**, is of special interest here: compound **3** reacts with 1 equiv. of water in an aprotic solvent and in the absence of base to give the air-stable hydrochloride **9**.

Compound **9** is crystalline; its structure was confirmed by NMR spectra and elemental analysis. In the ^{13}C NMR spectrum of the hydrochloride **9** a doublet at 97 ppm with a J_{CP} coupling constant of

TABLE 1 Yields, ^{31}P NMR, and Analytical Data

	<i>m.p.</i> ($^{\circ}\text{C}$); <i>b.p.</i> ($^{\circ}\text{C}$)	<i>Yield, g (%)</i>	<i>Formula</i>	$\delta^{31}\text{P}$ (<i>Solvent</i>)	<i>Found (Calculated) (%)</i>	
					<i>N</i>	<i>P</i>
3	94–98	2.20 (59)	$\text{C}_{16}\text{H}_{22}\text{Cl}_2\text{N}_3\text{OP}$	51.5 (benzene)	Cl 18.96 (18.95)	8.45 (8.27)
4	64–69	0.61 (73)	$\text{C}_{16}\text{H}_{24}\text{N}_3\text{O}_3\text{P}$	14.3 (dioxane)	12.20 (12.46)	9.10 (9.18)
5	Oil	0.44 (63)	$\text{C}_{17}\text{H}_{26}\text{N}_3\text{O}_3\text{P}$	28.5 (benzene)	11.80 (11.96)	8.75 (8.81)
6	92–94	0.52 (71)	$\text{C}_{16}\text{H}_{24}\text{N}_3\text{OPS}_2$	31.8 (acetonitrile)	11.52 (11.37)	8.25 (8.38)
7a	196–198	0.55 (65)	$\text{C}_{16}\text{H}_{26}\text{N}_5\text{OP}$	34.8 (THF)	20.33 (20.88)	9.12 (9.24)
7b	126–128	0.69 (77)	$\text{C}_{24}\text{H}_{42}\text{N}_5\text{OP}$	19.48 (benzene)	15.76 (15.65)	6.91 (6.92)
8	80–83	1.64 (78)	$\text{C}_{20}\text{H}_{36}\text{N}_7\text{OP}$	30.7 (benzene)	23.32 (23.26)	7.39 (7.35)
9	176–177	1.04 (53)	$\text{C}_{16}\text{H}_{24}\text{Cl}_2\text{N}_3\text{O}_2\text{P}$	36.6 (benzene)	Cl 17.92 (18.08)	7.78 (7.90)
11a	140	0.97 (54)	$\text{C}_{18}\text{H}_{25}\text{N}_4\text{O}_2\text{P}$	−2.0 (acetonitrile)	15.33 (15.55)	8.61 (8.60)
11b	123	1.27 (60)	$\text{C}_{23}\text{H}_{27}\text{N}_4\text{O}_2\text{P}$	−1.8 (benzene)	13.30 (13.26)	7.41 (7.33)
13	Oil	1.53 (48)	$\text{C}_{12}\text{H}_{13}\text{Cl}_2\text{N}_2\text{O}_2\text{P}$	18.8 (benzene)	8.70 (8.78)	9.65 (9.71)
14	69–73	1.60 (76)	$\text{C}_{20}\text{H}_{29}\text{N}_4\text{O}_4\text{P}$	17.8 (benzene)	13.27 (13.32)	7.40 (7.37)



204.7 Hz is observed. The reaction of **9** with triethylamine leads to the abstraction of hydrogen chloride. An intermediate diisopropylamino(oxo)phosphonio ylide **10** may play a role here, but attempts to confirm the formation of this compound of three-coordinate, pentavalent phosphorus by spectral methods failed.

However, when the dehydrochlorination reaction was conducted in the presence of aceto- or benzonitrile, it led to a new type of phosphorus-containing heterocyclic system, **11a** and **11b**, suggesting the formation of the extremely reactive ylide **10** as an intermediate. The structure of the bicyclic compounds

TABLE 2 ^1H NMR Data of Phosphorus-Containing Pyrazolonylides (δ , ppm; J , Hz)

	C^3CH_3	$PN-CH$	$NCHCH_3$	$o-Ph$	$m-Ph$	$p-Ph$	Other
3^a	2.29 s	3.41 dd (6.8, 25.4)	0.88 d (6.9)	8.79 d (8.0)	7.28 dd (7.8, 7.0)	6.94 m	
4^b	2.81 s	3.70 m	1.49 d (4.8)	7.64 s	7.64 s	7.64 s	OH 6.5 s
5^c	2.27 s	3.45 m	1.25 d (6.8)	7.89 d (8.0)	7.39 dd (7.8, 7.8)	7.18 dd (7.6, 7.8)	OCH ₃ 3.64 d (10)
6^b	2.81 s	3.68 m	1.48 d (6.6)	7.62 s	7.62 s	7.62 s	—SH, —OH 6.65 s
7a^b	2.68 s	3.64 m	1.43 d (5.8)	7.60 m	7.60 m	7.60 m	—NH 9.2 d (10.8)
7b^a	2.37 s	3.42 m	1.36 m	9.10 d (5.8)	7.32 m	6.94 dd (7.4, 6.2)	C(CH ₃) ₃ 1.05 s 0.85 s
8^c	2.24 s	3.82 m	1.30 d (7.0)	8.07 d (8.0)	7.33 dd (7.8, 8.0)	7.05 dd (7.6, 7.4)	—NH 9.94 d (11.2)
9^c	2.50 s	3.16 m	1.30 d (6.8)	7.70 d (7.4)	7.49 dd (7.8, 7.6)	7.35 dd (7.6, 7.2)	—NH 6.0 s
11a^a	2.56 s	2.92 m	1.26 dd (7.0, 7.8)	7.68 d (7.8)	7.10 dd (7.0, 7.9)	6.96 dd (7.0, 8.0)	N(CH ₃) ₂ 2.60 s
11b^c	2.55 s	3.23 m	1.33 m	7.77 d (7.6)			N=CCH ₃ 1.72 s
13^c	2.51 s			7.65 d (7.2)	7.50 m	7.42 dd (7.6, 7.4)	7.4–8.19 m C–Ph
14^c	2.41 s			7.40–7.73 m	7.40–7.73 m	7.40–7.73 m	OCH ₂ 4.16 q (7)
							OCH ₂ CH ₃ 1.29 t (7)
							OCH ₂ CH ₂ N 3.20 m,
							3.80 m OCH ₂ 4.08 q (7)
							OCH ₂ CH ₃ 1.25 t (7)

^aIn C₆D₆.

^bIn CD₃CN.

^cIn CDCl₃.

TABLE 3 ^{13}C NMR Data of Phosphorus-Containing Pyrazolonylides (δ , ppm; J , Hz)

	C^3	C^4	C^5	$\text{C}^3\text{-CH}_3$	PN-CH	$\text{CH-(CH}_3)_2$	<i>i</i> -Ph	<i>o</i> -Ph	<i>m</i> -Ph	<i>p</i> -Ph	Other
3^a	146.8d (16.3)	75.7d (188.5)	165.2d (29.3)	16.8d (1.5)	51.5d (3.6)	21.5d (3.5)	140.9s	118.9s	128.8s	123.6s	
7b^a	147.5d (14.9)	76.4d (189.1)	167.7d (25.8)	14.9s (14.9)	46.5d (6.2)	23.4s (6.2)	142.4s	119.0s	128.4s	122.5s	NCCH ₃ 51.9s 53.3s NCCH ₃ 31.9d (2.2)
11a^a	148.9d (5.0)	92.6d (168.2)	153.3d (8.9)	14.4s (5.0)	46.8d (6.1)	24.7d (2.7)	138.2s	121.5s	129.2s	126.8s	PN=C 151.5d (13.2) N=CCH ₃ 21.4s
11b^b	149.0d (5.1)	91.9d (171.1)	151.5d (7.2)	14.3s (5.1)	46.8d (6.0)	23.5d (2.5)	137.2s	122.2s	129.2s	127.6s	PN=C 151.1d (13.2) CPh 130.1s 128.8s 129.5s 133.2s

^aIn C₆D₆.^bIn CDCl₃.

11a and **11b** was confirmed by ^{31}P , ^1H , and ^{13}C NMR spectroscopy and by elemental analysis.

The structure of compound **11b** was unambiguously confirmed by a single crystal X-ray structure analysis. The structure of the molecule in the crystal is shown in Fig. 1.

The heterocyclic ring system is essentially planar (mean deviation from the least-squares plane: 0.029 Å) and subtends with the phenyl groups C(12)–C(17) and C(18)–C(23) interplanar angles of 23.1° and 16.4°, respectively. The geometry at phosphorus is tetrahedral, with bond angles from N(1)–P–C(4) 99.23(14)° to O(2)–P–C(4)

116.40(14)°. The atoms N(2) and N(4) display a planar configuration, with angle sums of 359.8° and 359.0°, respectively.

Considering the structure of the heterocycles obtained as a result of a [4 + 2]cycloaddition, it is more appropriate to describe **10** as a new type of acylmethylene(oxo)phosphonio ylide. Such compounds were not isolated previously [5], but their formation in some cases was confirmed by reaction with carbonyl compounds. Because of the formally conjugated system P=C–C=O, acylmethylene(oxo)phosphine ylides can act as heterodienes producing the [4 + 2]cycloaddition products [6], as in the present case. An attempt to synthesize a *P,P,P*-trichloropyrazolonylide was undertaken. In contrast to the case of the *P*-diisopropylamino-*P*-chloropyrazolyphosphine (**1**), the chlorination of the pyrazolyldichlorophosphine **A** is not accompanied by dealkylation, but leads to the formation of the stable tetrachlorophosphorane **12**, which was characterized as the phosphonic dichloride **13** and then transformed into the morpholide **14**.

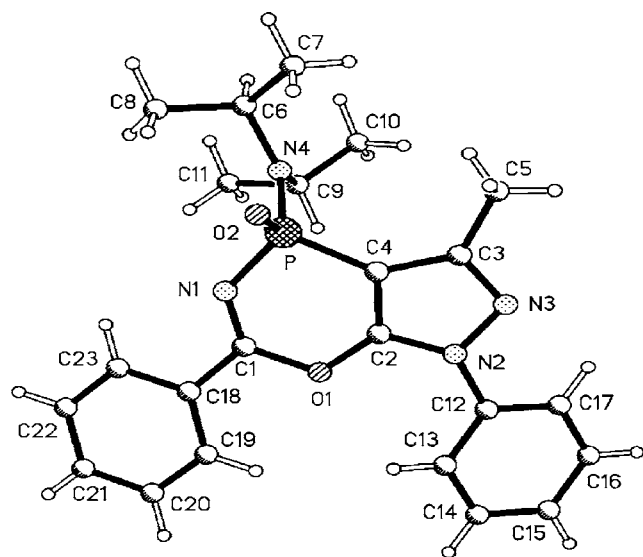
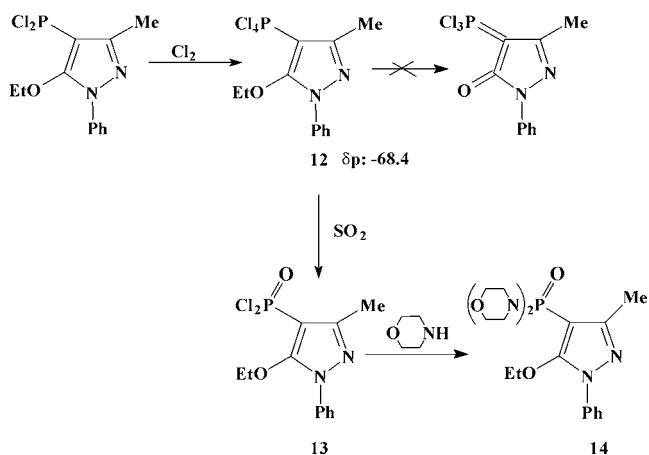
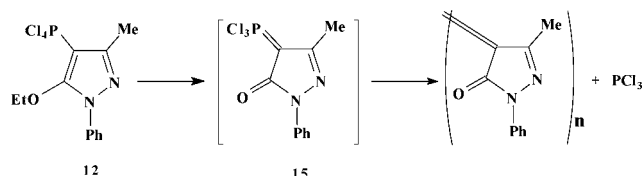


FIGURE 1 Structure of compound **11b** in the crystal (radii are arbitrary). Selected bond lengths (Å) and angles (°): P–O(2) 1.456(2), P–N(4) 1.638(3), P–N(1) 1.677(3), P–C(4) 1.757(3), O(2)–P–N(4) 112.98(15), O(2)–P–N(1) 111.51(14), N(4)–P–N(1) 106.90(14), O(2)–P–C(4) 116.40(15), N(4)–P–C(4) 108.65(15), N(1)–P–C(4) 99.23(14), C(9)–N(4)–P 117.9(2), C(6)–N(4)–P 122.5(2), C(2)–C(4)–P 119.8(2), C(3)–C(4)–P 136.7(3).



After the solution of compound **12** in methylene chloride was left at ~10°C for 2 h, a signal at 66 ppm

was seen in its ^{31}P NMR spectrum, which may be assigned to the *P,P,P*-trichloropyrazolonylide **15**. However, all attempts to isolate **15** as an individual compound or derivative led to breaking of the C–P bond, with formation of phosphorus trichloride and polymeric derivatives of pyrazolone.



Thus, as expected, *P,P*-dichloroylides are highly reactive compounds that can be used for the synthesis of various new types of pyrazole derivatives containing tetracoordinated phosphorus, or for obtaining new types of organic phosphorus compounds. The further development of phosphorus dichloroylide chemistry is of particular interest because of the expanding possibilities for the synthesis of new phosphorus-containing heterocyclic systems.

EXPERIMENTAL

The ^{31}P NMR spectra were recorded on a Varian UnityPlus 300 NMR spectrometer at 121 MHz. Chemical shifts are reported relative to 85% H_3PO_4 as an external standard. ^1H and ^{13}C NMR spectra were recorded on the same instrument at 300 MHz for ^1H and 75 MHz for ^{13}C .

4-Dichloro(diisopropylamino)phosphonio-[5(4H)oxopyrazol-4-ylide-5-one] (**3**)

To a solution of the dichlorophosphine **A** (3.03 g; 10 mmol) in 10 ml of benzene a solution of diisopropylamine (2.5 g; 25 mmol) in 10 ml of petroleum ether was added. After 6 days a signal at 109.2 ppm, corresponding to **1**, in the ^{31}P NMR spectrum was seen. The precipitate was filtered off, the solvent was removed from the filtrate, and the oily residue was dried in vacuo. The residue was dissolved in 10 ml of petroleum ether, and a solution of chlorine (1.06 g; 15 mmol) in 10 ml CCl_4 was added at 10°C . After 24 h the precipitate thus formed was filtered off and purified by recrystallization from 10 to 15 ml heptane.

5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl-*N,N*-diisopropylphosphonamidic Acid (**4**)

To a solution of the *P,P*-dichloroylide **3** (0.94 g; 2.5 mmol) in 10 ml of dioxane a mixture of water (0.09 g; 5 mmol) and triethylamine (0.55 g; 5.5 mmol)

in 7 ml of dioxane was added. After 3 days the precipitate was filtered off and the solvent was removed from the filtrate in vacuo. The residue was dissolved in benzene on heating, and the transparent solution was separated from a small quantity of an oily product. The solvent was removed in vacuo. The residue was treated with diethyl ether to give a powder.

Methyl 5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl-*N,N*-diisopropylphosphonamidate (**5**)

To a solution of the *P,P*-dichloroylide **3** (0.75 g; 2 mmol) in 10 ml of benzene a mixture of methanol (0.13 g; 4 mmol) and triethylamine (0.44 g; 4.4 mmol) in 5 ml of benzene was added. The precipitate formed within 1 day and was removed by filtration from the reaction mixture. The solvent was removed in vacuo. The product was purified by precipitation from benzene with petroleum ether.

5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl-*N,N*-diisopropylphosphonamidodithioic Acid (**6**)

To a solution of the *P,P*-dichloroylide **3** (0.75 g; 2 mmol) in 7 ml of acetonitrile a solution of sodium hydrosulfide (0.22 g; 4 mmol) in 7 ml of acetonitrile was added. The reaction mixture was stirred for 10 h, the precipitate was filtered off, the solvent was removed in vacuo, and the product was isolated from the residue by recrystallization from 5 to 7 ml of decane.

5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl-*N,N*-diisopropylphosphonimidic Diamide (**7a**)

The *P,P*-dichloroylide **3** (0.94 g; 2.5 mmol) was added to 5 g (294 mmol) of liquid ammonia at -40°C . The reaction mixture was kept at this temperature for 6 h. After the ammonia was evaporated, the reaction mixture was dissolved in 10 ml of methylene chloride. The precipitate was filtered off and the solvent was removed in vacuo. The residue was dissolved in 12 ml of THF, and the precipitate was again filtered off. The solvent was removed under reduced pressure. The residual oil was treated with diethyl ether to give a powder.

N',N''-Di(*tert*-butyl)-5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl-*N,N*-diisopropylphosphonimidic Diamide (**7b**)

To a solution of the *P,P*-dichloroylide **3** (0.75 g; 2 mmol) in 7 ml of benzene a mixture of

tert-butylamine (0.3 g; 4 mmol) and triethylamine (0.6 g; 6 mmol) in 10 ml of benzene was added. After 4 days the precipitate formed was filtered off, the solvent from the reaction mixture was removed in vacuo, and the residue was dried in vacuo. The oily residue solidified on standing and was washed with petroleum ether and dried.

*4-[(Diisopropylamin(2,2-dimethylhydrazino)-dimethylphosphorohydrazonoyl]-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (8)*

To a solution of the *P,P*-dichloroylide **3** (1.87 g; 5 mmol) in 20 ml of benzene a mixture of *N,N*-dimethylhydrazine (0.6 g; 10 mmol) and triethylamine (1 g; 10 mmol) in 10 ml of benzene was added. After 1 h the precipitate was filtered off, the solvent was removed from the filtrate in vacuo, and the residue was dissolved in 15 ml of benzene. The product was isolated from the solution by precipitation with portions of 7 ml of petroleum ether and was crystallized from 15 ml of octane.

*5-Hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl-*N,N*-diisopropylphosphonamidic Chloride Hydrochloride (9)*

To a solution of the *P,P*-dichloroylide **3** (1.87 g; 5 mmol) in 10 ml of acetonitrile a solution of water (0.09 g; 5 mmol) in 5 ml of acetone was added. The mixture was heated, and a colorless precipitate was immediately formed. After 0.5 h the precipitate was filtered off. The product was purified by recrystallization from a mixture of dichloromethane/benzene (3:10).

*1-(Diisopropylamino)-3,8-dimethyl-5-phenyl-1,5-dihydro-1 λ^5 -pyrazolo[4,3-*e*][1,3,4]-oxazaphosphorin-1-one (11a)*

To a solution of the *P,P*-dichloroylide **3** (1.87 g; 5 mmol) in 30 ml of acetonitrile a mixture of water (0.09 g; 5 mmol) and triethylamine (1 g; 10 mmol) was added. The precipitate formed was filtered off and was dissolved in benzene. A newly formed precipitate was filtered off, and the solvent was removed from the filtrate in vacuo. The product was obtained from the residue by recrystallization from 15 ml of heptane.

*1-(Diisopropylamino)-8-methyl-5,8-diphenyl-1,5-dihydro-1 λ^5 -pyrazolo[4,3-*e*][1,3,4]-oxazaphosphorin-1-one (11b)*

To a solution of the *P,P*-dichloroylide **3** (1.87 g; 5 mmol) in 20 ml of benzonitrile a mixture of water

(0.09 g; 5 mmol) and triethylamine (1 g; 10 mmol) was added. The solvent was removed in vacuo after 24 h, and toluene was added to the residue. The precipitate of triethylamine hydrochloride was filtered off. The product was obtained by crystallization from 10 to 15 ml of a mixture of heptane/benzene (2:1).

*5-Ethoxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl-phosphonic Dichloride (13)*

To a solution of the dichlorophosphine A (3.03 g; 10 mmol) in 20 ml of benzene a solution of chlorine (0.85 g; 12 mmol) in 25 ml of carbon tetrachloride was added dropwise with stirring within 1 h at -30°C . At that temperature the reaction mixture was stirred for 1 h, and then it was allowed to warm to ambient temperature. The ^{31}P NMR spectrum of the reaction mixture revealed a signal at -68.4 ppm corresponding to the tetrachlorophosphorane **12**. SO_2 was bubbled through the reaction mixture for 0.5 h. The solvent was removed under reduced pressure. The residue was dissolved in petroleum ether and filtered. The solvent was evaporated, and the residue was dried in vacuo.

*4-[(5-Ethoxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(4-morpholinyl)phosphoryl]morpholine (14)*

Morpholine (1.75 g; 20 mmol) in 15 ml of benzene was added to a solution of **13** (1.6 g; 5 mmol) in 15 ml of benzene. After 2 h the morpholine hydrochloride formed was filtered off. The solvent was evaporated under reduced pressure and a solid residue was left. The product was purified by reprecipitation with heptane from benzene.

X-Ray Structure Determination of 11b

Crystal data: Monoclinic, space group $P2_1/c$, $a = 7.950(2)$, $b = 15.651(3)$, $c = 18.370(4)$ Å, $\beta = 99.79(3)^{\circ}$, $U = 2252.9$ Å³, $Z = 4$, $D_x = 1.246$ Mg m⁻³, $F(000) = 896$, $\mu = 0.15$ mm⁻¹, $T = -100^{\circ}\text{C}$.

Data collection: A crystal ca. $0.8 \times 0.4 \times 0.35$ mm was used to register 4288 intensities (Mo K α radiation, $2\theta_{\text{max}} 50^{\circ}$) on a Stoe STADI-4 diffractometer.

Structure refinement: The structure was refined anisotropically against F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen) to $wR2$ 0.059, $R1$ 0.151 for 276 parameters and 3979 independent reflections; max. $\Delta\rho = 0.49$ eÅ⁻³, $S = 1.07$. Hydrogen atoms were included using a riding model or rigid methyl groups.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC-186668. Copies can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: Int. ++1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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