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Dealkylation of 4-Phosphorylated 5-Alkoxypyrazoles: Easy Synthetic Access to P-Chloro Ylides

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ABSTRACT

The chlorination of 5-alkoxypyrazoles containing bis-(dialkylamino)- or diphenylphosphino groups at the 4-position afforded highly unstable chlorophosphonium chlorides that dealkylated giving chlorobis(dialkylamino)- and chlorodiphenylphosphonium(3-methyl-5-oxo-1-phenyl-5H-pyrazol-4-yl)ides. The P-chloro ylides do not react with aromatic aldehydes, but chlorine atoms are easily substituted with OH, NH_2 ArNH, and Et_2N residues. They also exhibit basic properties and add hydrogen chloride with protonation at N-2. © 1998 John Wiley & Sons, Inc. Heteroatom Chem **9**:41–49, 1998

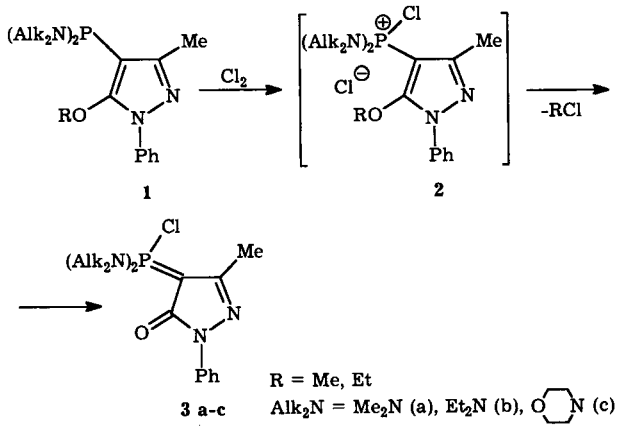
INTRODUCTION

Previously, we discovered and studied the rearrangement of 5-alkoxy-4-phosphorylpyrazoles to triorganylpyrazolone ylides, which involved migration of an alkyl group from the oxygen atom to the trivalent phosphorus atom or dealkylation of 5-alkoxy-4-phosphoniopyrazolyl halides [1].

The present study focuses on the applicability of this rearrangement to the synthesis of P-chloropyrazolone ylides. P-halogeno ylides are known to offer new synthetic potentialities for phosphorus ylides and therefore have attracted increasing experimental and theoretical interest [2].

RESULTS AND DISCUSSION

It has been found that the chlorination (with chlorine or hexachloroethane) of 5-alkoxypyrazoles **1** containing diaminophosphino groups at position **4** leads to stable chloro ylides **3a–c** rather than to the expected chlorophosphonium halides **2.** The dealkylation occurs so rapidly that the latter compounds cannot be detected at 20°C even by ^{31}P NMR spectroscopy.



1 2 3 a-c

Dedicated to Prof. William McEwen on the occasion of his seventy-fifth birthday.

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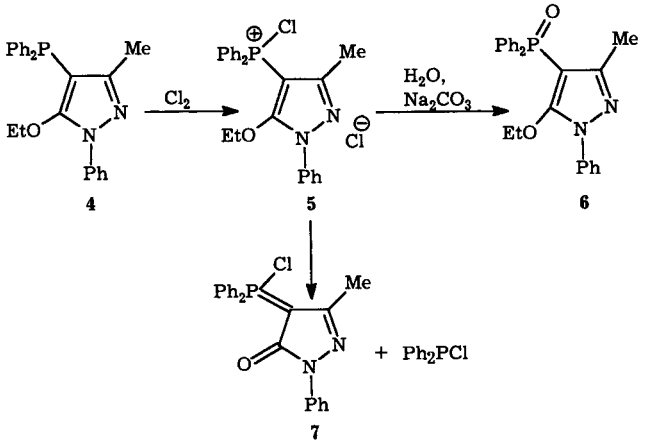
Contrary to the behavior of compounds **1**, phosphine **4**, when chlorinated, provided a rather stable chlorophosphonium salt **5** that could not be isolated in a pure state, although its structure was supported by ^{31}P NMR spectral data as well as by hydrolyzing it to the phosphine oxide **6**.

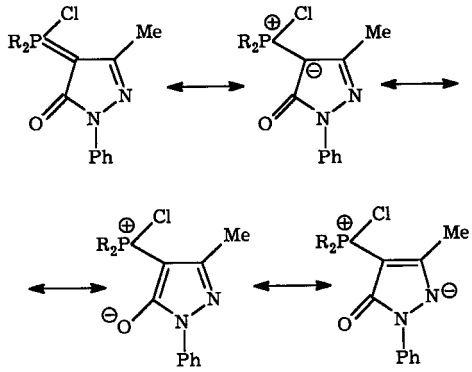


4 **5** **6** **7**

When the chlorophosphonium salt **5** was maintained at 20°C in benzene for 24 hours, it decomposed to give the chloro ylide **7** and diphenylchlorophosphine. The decomposition probably involves, among other routes, P–C bond cleavage, as for *p*-dimethylaminophenyltetrachlorophosphorane [3].

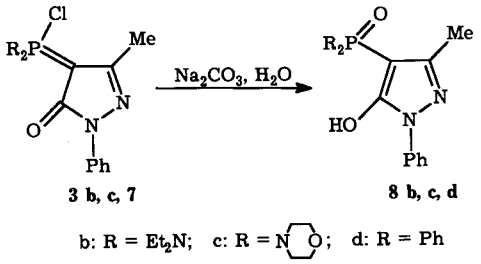
P-Chloro ylides **3a–c** and **7** (see Table 1) were obtained as solid substances that could be crystallized from octane and were stable when kept in a dry, inert atmosphere. Their structures were corroborated by ^{1}H, ^{13}C, and ^{31}P NMR spectra (see Tables 1–3). The carbon atom of the P=C groups shows ^{13}C NMR signals in the range of δ = 78–87 that appear as doublets with coupling constants J_{cp} of about 120 Hz, consistent with literature data [4]. IR spectra of the chloro ylides revealed the carbonyl vibration band at 1626–1670 cm^{-1} and a band at 1250 cm^{-1} that can be assigned to the valence vibration (ν) of the P=C group.

Reactions with carbonyl compounds are known to be typical of P-halogeno ylides. In our case, attempts to use the P-chloro ylides obtained in Wittig reactions with *p*-nitrobenzaldehyde, *p*-dimethylaminobenzaldehyde, and *p*- cholorophenyl isocyanate proved to be unsuccessful. Even when permitted to stand at room temperature for long periods, no reaction products were observed in the mixture of reagents. The reluctance of P-chloro ylides to react with carbonyl compounds is apparently due to a notable delocalization of the negative charge of the ylide carbon atom into the pyrazolone moiety.



The absence of P–C chlorotropy in molecules of the chloro ylides under consideration is attributable to the same reason.

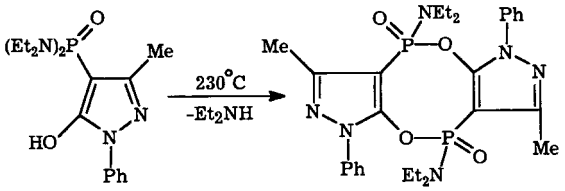
P-chloro ylides are readily hydrolyzed by atmospheric moisture or by reaction with aqueous sodium carbonate to give the corresponding phosphonates **8**. These colorless crystalline solids have been assigned structures consistent with data of elemental analyses and NMR spectra (see Tables 1 and 2).



3 b, c, 7 **8 b, c, d**

b: R = Et_2N; c: R = ; d: R = Ph

Compound **8b** was found to display unusual chemical behavior: On heating it to 230°C under vacuum, one of the diethylamino groups was eliminated to give, according to mass and NMR (^{31}P, ^{1}H, and ^{13}C) spectra, a tricyclic compound **9**.



8 b **9**

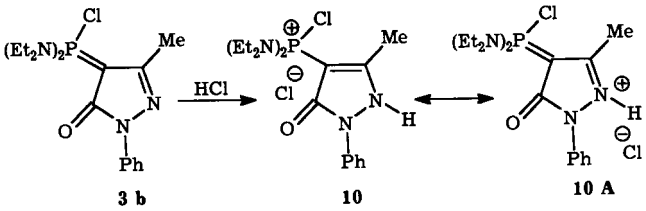
A similar method for generating metaphosphates by thermal splitting of alkylamidophosphoric acids in inert solvents was elaborated by Quin et al. in 1991 [5].

The P-chloro ylides under consideration here manifest basic properties and readily add hydrogen chloride. For instance, chloro ylide **3b** reacts with

TABLE 1 Yields, Constants, Data of Elemental Analyses, and ^{31}P NMR Spectral Parameters for Chloropyrazolone Ylides and Their Derivatives **3a–14c**

	Mp (°*C*)	*Yield* (%)	*Formula*	^{31}P (*solvent*)	*Found, %* (*Calculated, %*)	
					N	*P*
3a	130–133	65	$C_{14}H_{20}ClN_4OP$	65.2 (chloroform)	17.20 (17.14)	9.67 (9.48)
3b	87–92	73	$C_{18}H_{28}ClN_4OP$	60.7 (chloroform)	14.15 (14.63)	8.61 (8.09)
3c	107–112	51	$C_{18}H_{24}ClN_4O_3P$	57.1 (benzene)	13.20 (13.64)	7.91 (7.54)
6	112–115	65	$C_{24}H_{23}N_2O_2P$	19.11 (chloroform)	7.10 (6.96)	7.69 (7.70)
7	87–90	39	$C_{22}H_{18}ClN_2OP$	52.5 (chloroform)	7.03 (7.13)	7.84 (7.88)
8b	120	58	$C_{18}H_{29}N_4O_2P$	29.5 (chloroform)	14.93 (15.37)	8.49 (8.50)
8c	123–126	67	$C_{18}H_{25}N_4O_4P$	26.1 (chloroform)	14.42 (14.28)	7.90 (7.89)
8d	101–103	87	$C_{22}H_{19}N_2O_2P$	31.2 (chloroform)	7.43 (7.48)	8.40 (8.27)
9	111–112	55	$C_{28}H_{36}N_6O_4P_2$	17.9 (chloroform)	14.61 (14.43)	10.47 (10.64)
10	152	91	$C_{18}H_{29}Cl_2N_4OP$	56.1 (chloroform)	13.41 (13.36)	7.34 (7.39)
12b	173–174	69	$C_{18}H_{30}N_5OP$	43.8 (chloroform)	19.11 (19.27)	8.14 (8.52)
12c	125–127	53	$C_{18}H_{26}N_5O_3P$	39.7 (chloroform)	17.94 (17.89)	8.35 (7.91)
13a	85–87	65	$C_{18}H_{30}N_5OP$	31.3 (benzene)	18.95 (19.27)	8.21 (8.52)
14a	oil	47	$C_{20}H_{26}N_5OP$	38.1 (benzene)	17.99 (18.26)	8.32 (8.08)
14c	72–75	41	$C_{25}H_{32}N_5O_3P$	33.0 (benzene)	14.49 (14.54)	6.50 (6.43)

hydrogen chloride to furnish a colorless crystalline phosphonium salt **10,** stable in the air.



The structure of **10** was established by a single-crystal X-ray diffraction study. The perspective view of molecule **10** with its atom-numbering scheme is shown in Figure 1. Table 4 contains selected intramolecular bond distances and angles.

The phosphorus atom has a distorted tetrahedral bond configuration: the Cl-P-N and Cl-P-C(1) bond angles are reduced to 105.6–107.6(1)°, whereas the N-P-N and N-P-C bond angles are increased to 111.3–113.0(2)°. The P–N bonds of 1.600(2) and 1.614(2) Å are slightly shorter than the P–N bonds in $[MeP(NEt_2)_3]^+$ [1.625–1.633(3), avg. 1.628 Å] [6] and related phosphorus cations [7] but quite comparable with the corresponding values of 1.584–1.605(5), avg. 1.600 Å observed in $[F_3C–P(NMe_2)_3]^+$ and $[F_3C–P(NEt_2)_3]^+$ [8]. This effect reflects the electron-withdrawing capacity of the halogen-containing substituents for lowering the energy of the outer phosphorus orbitals and thus promoting more effective bonding toward nitrogen.

The nitrogen atoms N(1), N(2), N(3), and N(4) in **10** have trigonal planar geometry (the sum of bond angles is 360° within the experimental error limits). The PC(1–5)N(1)N(2)O bond system is essentially planar [the deviations from the least-squares plane not exceeding 0.056(4) Å]. The geometrical parameters of the N(1)N(2)C(1–3) heterocycle indicate considerable delocalization of the electron density:

TABLE 2 ^{1}H NMR Spectral Data (δ, Multiplicity, and *J*, Hz) for Chloropyrazolone Ylides and Their Derivatives

	3-CH_3	*N–$CH_{2,3}$*	*N-C-$CH_{2,3}$*	*o-Ph*	*m-Ph*	*p-Ph*	*Other Groups*
3a[a]	2.25s	2.89d (12.6)	—	7.8d (8.6)	7.3t (8.4)	7.1t (8.4)	
3b[a]	2.45s	3.32m (23.6)	1.12t (7.4)	7.9d (7.6)	7.4t (7.2)	7.2t (7.6)	
3c[b]	2.33s	3.38m	3.79m		7.35–7.95m		
6	2.17	3.8q[e] (7.0)	1.18t[e] (7.0)		7.30–7.94m		
7[a]	2.11s	—	—		7.37–7.91m		
8b[a]	2.31s	3.15m (7.2)	1.13t (7.3)	7.8d (7.6)	7.4t (7.6)	7.3t (7.8)	5-OH 4.22s
8c[a]	2.28s	3.20t	3.70t		7.21–7.92m		
8d[a]	2.36s	—	—		7.20–8.00m		
9[a]	2.34s	2.74d.d. (35.2)	0.85t (7.0)	7.75d (7.0)	7.71t (7.2)	7.36t (7.3)	
10[c]	2.70s	3.35q (7.0)	1.29t (7.0)	7.9m	7.5t	7.3m	NH 12.38s
11c[d]	2.24s	3.21m	3.70m	7.71d (8.1)	7.39t (8.0)	7.18t (7.8)	P–NH_2 5.49s, OH 4.88s
12b[a]	2.19s	3.15m (7.2)	1.14t (7.2)	8.1d (7.8)	7.3t (7.8)	7.1t (7.8)	P–NH_2 5.07m
12c[a]	2.22s	3.67t	3.15t	8.0d	7.09–7.38m		NH{OH} 5.6 braod s
13a[b]	2.27s	2.70d, 2.79m (10.6)	1.35t (7.0)	7.8d (7.2)	7.4t (7.2)	7.2t (7.2)	
14a[b]	2.25s	2.75d (16.0)	—		6.61–7.46m		NH–Ph, 11.04d (11)
14c[b]	2.30s	3.25m	3.63t	8.0d (7.0)	7.4t (7.0)		7.00–7.17m NH{OH} 11.45d

[a]$CDCl_3$.
[b]C_6D_6.
[c]CD_3CN.
[d]CD_3OD.
[e]OEt.

TABLE 3 ^{13}C NMR Spectral Data (δ, Multiplicity, and J_{cp}, Hz) for Chloro Ylides and Their Derivatives (in $CDCl_3$)

	C-3	*C-4*	*C-5*	*i-Ph*	*o-Ph*	*m-Ph*	*p-Ph*	*3-CH_3*	*N–CH_2*	*C–CH_3*
3a	139.12d (4.4)	80d (122)	148.69d (12.2)	139.8s	120.3s	128.8s	125.1s	15.4d (35)	37.3s 36.1s	
3b	148.13d (6.2)	87.00d (126)	159.80d (13.0)	138.2s	120.7s	128.9s	126.0s	14.9s	39.7d (3.4)	13.5d (2.3)
7	149.67d (6.3)	87.78d (127)	160.39d (12.0)	134.7 134.3 133.7	132.4 131.7 131.4	131.3 129.7 129.0	130.0 129.4	14.0s		
9	148.06d (5.8)	86.94d (119)	159.81d (13.1)	138.2s	120.8s	128.9s	126.0s	14.9	38.3d (3.2)	13.7d (2.2)
12b	148.09d (8.8)	73.81d (121)	167.40d (16.3)	140.5s	119.4s	128.4s	123.3s	15.9s	39.4d (3.3)	13.7d (1.4)

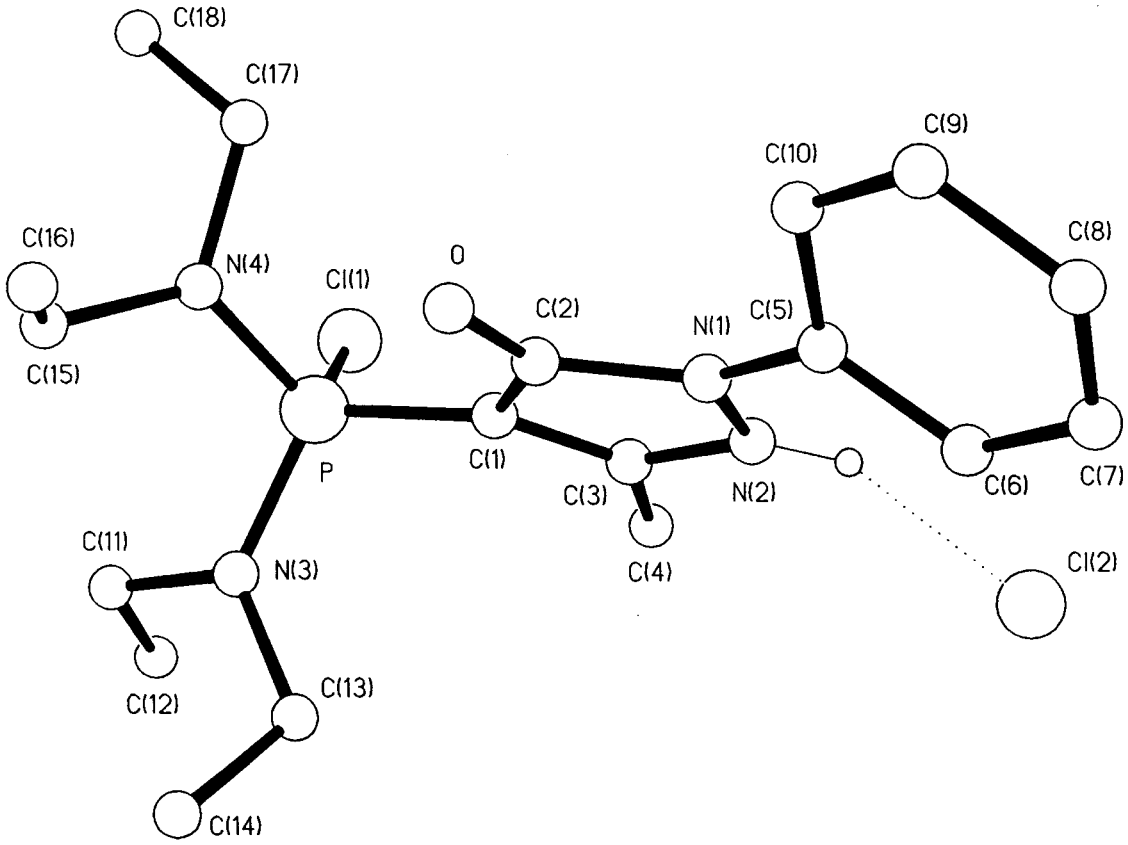


FIGURE 1 The perspective view of molecule 10 with its atom-numbering scheme.

TABLE 4 Selected Interatomic Distances and Angles in **10**

Bond Length (*Å*)		*Bond Angle* (°)	
Cl(1)–P	2.0236(8)	Cl(1)–P–N(3)	107.6(1)
P–N(3)	1.614(2)	Cl(1)–P–C(1)	105.6(1)
P–N(4)	1.600(2)	Cl(1)–P–N(4)	106.2(1)
P–C(1)	1.725(2)	N(3)–P–N(4)	111.3(1)
O–C(2)	1.238(3)	N(3)–P–C(1)	112.6(2)
N(1)–C(2)	1.402(3)	N(4)–P–C(1)	113.0(2)
N(1)–N(2)	1.377(3)	N(2)–N(1)–C(2)	109.4(2)
N(1)–C(5)	1.408(3)	N(2)–N(1)–C(5)	122.5(2)
N(2)–C(3)	1.324(3)	C(2)–N(1)–C(5)	128.0(2)
C(1)–C(2)	1.450(3)	N(1)–N(2)–C(3)	109.7(2)
C(1)–C(3)	1.395(3)	P–C(1)–C(2)	124.2(2)
		P–C(1)–C(3)	128.6(2)
		C(2)–C(1)–C(3)	107.2(2)
		O–C(2)–N(1)	124.1(2)
		O–C(2)–C(1)	131.6(2)
		N(1)–C(2)–C(1)	104.3(2)
		N(2)–C(3)–C(1)	109.5(2)
		N(2)–C(3)–C(4)	119.4(3)
		C(1)–C(3)–C(4)	131.2(2)

the C(1) = C(3) bond of 1.395(3) Å is significantly elongated, whereas the C(3)–N(2), N(2)–N(1), and N(1)–C(2) bonds are shortened to 1.324(3), 1.377(3), and 1.402(3) Å, (the standard values for $C(sp^2)=C(sp^2)$, $N(sp^2)$–$N(sp^2)$ and $C(sp^2)$–$N(sp^2)$ bonds being 1.33, 1.41, and 1.45 Å, respectively [9]). On the other hand, the P–C(1) bond length of 1.725(2) Å in **10** is ordinary for phosphorus ylides $R_3P=CR'$. Therefore, the bonding features of **10** may be described by a pronounced contribution of the resonance form **10A.**

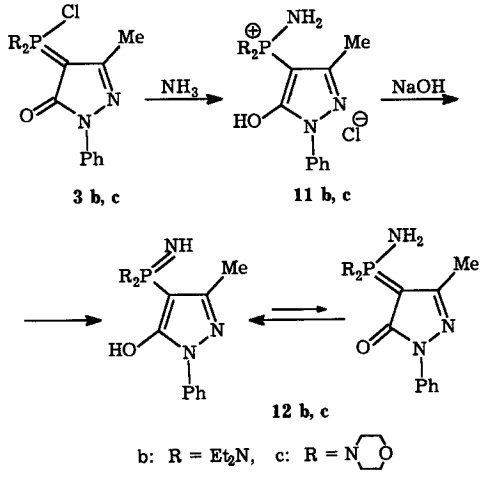
The shortening of the N(1)–C(5) bond to 1.408(3) Å indicates the conjugation between the pyrazolone and phenyl rings [the dihedral angle between these rings being 32.8(1)°].

A specific feature of the crystal structure of compound **10** is the hydrogen bond N(2)–H. . .Cl(2) between the cation and anion (the value of the N(2). . .Cl(2) distance of 2.961 Å being considerably

shorter than the average statistical value of 3.23 Å, typical for H bonds of this type [10]).

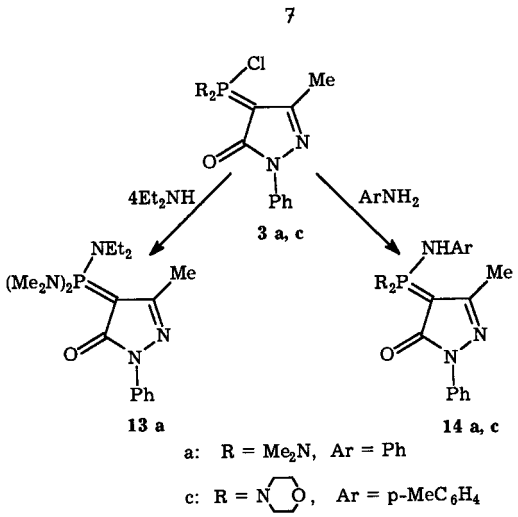
The chlorine atom in the molecules of ylides **3** notably slows their rate of alkylation compared to that of analogous alkyl ylides. Thus, on keeping compound **3b** in contact with methyl iodide at 20°C for over 15 days, the strongest ^{31}P resonance still originates from the chloro ylide, while the alkylation of the analogous pyrazolone ylide containing an alkyldiaminophosphonium group is complete within 20 hours [1].

Under the action of gaseous ammonia, chlorine atoms in the chloro ylides are readily (in 1 h at room temperature) displaced by amino groups to produce iminophosphonates. The structures of the resulting products are supported by ^{31}P and ^{1}H NMR spectroscopy and by elemental analyses (see Tables 1 and 2).



Compounds **12** exist predominantly in the phosphazo form, which is consistent with their IR spectra exhibiting no carbonyl band at 1600 cm^{-1}.

The ease of substitution of the chlorine atom in chloro ylides by a dialkylamino or an arylamino group is mainly governed by steric effects of substituents at the phosphorus atom. In the case of dimethylamino groups bonded to the phosphorus atom (compound **3a**), the reaction with diethylamine and aniline carried out at 20°C requires 24 hours to reach completion, whereas in the molecule of chloro ylide **3b,** the chlorine is not substituted even on boiling the reaction mixture for a long period. For compound **3c,** the time required for substitution of the chlorine by a *p*-toluidino residue in the presence of triethylamine is as long as 1 week.



Thus, although P-chloro pyrazolone ylides proved to be inert to carbonyl compounds, they are undoubtedly of promise in synthetic applications, due to the mobile character of the chlorine at the phosphorus atom.

EXPERIMENTAL

All manipulations with phosphorus compounds were carried out in purified anhydrous solvents under argon.

^{31}P NMR spectra were measured using a Varian VXR-300 (at 121.42 MHz), with 85% aqueous H_3PO_4 as an external reference.

^{1}H and ^{13}C NMR spectra were measured using a Varian VXR-300 (at 300 and 75.35 MHz) instrument, with TMS as an internal reference.

X-Ray Crystal Structure Determination of **10**

Crystal data: $C_{18}H_{29}Cl_2N_4OP$, M = 419.3, monoclinic, a = 8.927(7), b = 12.142(3), c = 9.882(3) Å, β = 98.36(4)°, V = 1059(1) $Å^3$, Z = 2, d_c = 1.31 g cm^{-3}, space group $P2_1$, μ = 36.5 cm^{-1}, F(000) = 444.

Crystallographic measurements were made at ambient temperature (18°C) using an Enraf Nonius CAD-4 diffractometer operating in the $\omega/2\theta$ scan mode (the ratio of the scanning rates $\omega/2\theta$ = 1.2). The intensity data were collected within the range $1 \leq \theta \leq 66°$ using graphite monochromated Cu-K_α radiation (λ = 1.54184 Å). Intensities of 2085 reflections (1955 unique reflections, R_{merge} 0.032) were measured. The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation. In the refinement, 1797 reflections with $I > 3\sigma(I)$ were used. The hydrogen atoms were placed in calculated positions and included in the final refinement with the

fixed positional and thermal (B_{iso} = 6 Å^2) parameters. Convergence was obtained at R = 0.045, R_w = 0.060, and GOF = 2.68 (234 refined parameters; largest shift/esd after final cycle <0.12; the largest peak in the final difference map, 0.31 e/Å^3). The weighting scheme was based on counting statistics and included a factor (p = 0.04) to downweight the intense reflections. Corrections for Lorentz and polarization effects but not for absorption were applied. All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package [11]. Atomic coordinates are listed in Table 5. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre [12].

Chlorobis(dimethylamino)phosphonium(3-methyl-5-oxo-1-phenyl-5H-pyrazol-4-yl)ide (**3a**). To a solution of 3-methyl-1-phenyl-5-ethoxypyrazolyl-4-phosphonous tetramethyldiamide (0.005 mol) in petroleum ether (10 mL), a solution of chlorine (0.005 mol) in carbon tetrachloride was added. The resulting oil settled out and crystallized on standing. The product was purified by crystallization from *n*-octane.

Chlorobis(diethylamino)phosphonium(3-methyl-5-oxo-1-phenyl-5H-pyrazol-4-yl)ide (**3b**). This compound was prepared analogously to **3a,** starting from 3-methyl-1-phenyl-5-ethoxypyrazolyl-4-phosphonous tetraethyldiamide.

TABLE 5 Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors B_{eq} (Å^2)

Atom	*x*	*y*	*z*	B_{eq}
Cl(1)	0.7177(1)	0.213	0.75326(9)	3.83(2)
Cl(2)	1.07502(9)	0.6638(1)	0.5325(1)	4.36(2)
P	0.67571(8)	0.34258(8)	0.87095(7)	2.40(1)
O	0.5035(3)	0.5808(3)	0.8197(3)	4.33(5)
N(1)	0.6815(3)	0.6241(3)	0.6769(3)	2.79(5)
N(2)	0.8082(3)	0.5736(2)	0.6412(3)	2.57(5)
N(3)	0.7875(3)	0.3326(3)	1.0142(3)	3.22(5)
N(4)	0.5022(3)	0.3319(3)	0.8928(3)	2.80(5)
C(1)	0.7109(4)	0.4583(3)	0.7793(3)	2.57(5)
C(2)	0.6161(4)	0.5557(3)	0.7666(3)	2.84(6)
C(3)	0.8267(3)	0.4762(3)	0.7012(3)	2.65(5)
C(4)	0.9602(4)	0.4076(4)	0.6812(4)	3.65(7)
C(5)	0.6384(3)	0.7317(3)	0.6349(3)	2.56(6)
C(6)	0.7473(4)	0.8096(3)	0.6138(4)	3.25(6)
C(7)	0.7024(5)	0.9162(4)	0.5779(4)	3.92(7)
C(8)	0.5545(6)	0.9466(4)	0.5617(4)	4.50(9)
C(9)	0.4433(4)	0.8663(4)	0.5766(4)	3.93(7)
C(10)	0.4851(4)	0.7605(3)	0.6133(3)	3.26(7)
C(11)	0.7970(5)	0.2251(4)	1.0858(4)	4.16(8)
C(12)	0.9397(7)	0.1633(5)	1.0741(6)	7.3(1)
C(13)	0.8941(5)	0.4160(5)	1.0710(5)	5.1(1)
C(14)	0.8788(8)	0.4495(5)	1.2146(5)	8.4(1)
C(15)	0.4485(4)	0.3360(5)	1.0275(4)	4.17(8)
C(16)	0.3563(7)	0.4348(6)	1.0477(5)	7.2(1)
C(17)	0.3849(4)	0.3239(4)	0.7712(4)	3.98(8)
C(18)	0.3018(6)	0.2148(6)	0.7644(6)	6.5(1)

Chlorodimorpholinophosphonium(3-methyl-5-oxo-1-phenyl-5H-pyrazol-4-yl)ide (**3c**). To a solution of 3-methyl-1-phenyl-5-ethoxypyrazolyl-4-phosphonous dimorpholide (0.004 mol) in a mixture of benzene (5 mL) and petroleum ether (5 mL) a solution of chlorine (0.004 mol) in benzene (10 mL) was added. The oil that settled out solidified on standing and was purified by crystallization from *n*-octane.

Diphenyl(3-methyl-1-phenyl-5-ethoxypyrazol-4-yl)phosphine Oxide (**6**). To a solution of diphenylphosphine **4** (0.01 mol) in benzene (7 mL), a solution of chlorine (0.01 mol) in carbon tetrachloride was added. The oil that settled out was separated 5 minutes later and dissolved in benzene. The ^{31}P resonance originating from chlorodiphenyl[4-(3-methyl-1-phenyl-5-ethoxypyrazolyl]phosphonium chloride **5** was detected at δ = 50.7. The benzene solution was shaken with saturated aqueous sodium carbonate (15 mL). Then the organic layer was separated and dried over sodium sulfate, and the solvent was evaporated to dryness. The residue was recrystallized from decane.

Chlorodiphenylphosphonium(3-methyl-5-oxo-1-phenyl-5H-pyrazol-4-yl)ide (**7**). To a solution of the diphenylphosphine **4** (0.008 mol) in benzene (10 mL), a solution of chlorine (0.008 mol) in benzene (10 mL) was added. The oil that first settled out dissolved after a time, and a crystalline solid precipitated from the reaction mixture within 24 hours. The precipitate was filtered off, washed with benzene, and dried.

Diphenyl(5-hydroxy-3-methyl-1-phenylpyrazol-4-yl)phosphine Oxide (**8d**). The chlorodiphenyl pyrazolone ylide **7** (0.001 mol) was dissolved in methylene chloride (7 mL) and shaken with saturated aqueous sodium carbonate (10 mL). The organic layer was washed with water and dried over sodium sulfate. The solvent was evaporated to dryness, and the residue was recrystallized from *n*-hexane.

5-Hydroxy-3-methyl-1-phenylpyrazolyl-4-phosphonic Tetraethyldiamide (**8b**). The chloro ylide **3b** (0.005 mol) was dissolved in methylene chloride (20 mL) and shaken with saturated aqueous sodium carbonate (30 mL). The organic layer was washed with water (2 × 30 mL) and dried over sodium sulfate. The solvent was evaporated to dryness, and the res-

idue was rubbed in diethyl ether with cooling, and then the solid product was recrystallized from *n*-heptane.

5-Hydroxy-3-methyl-1-phenylpyrazolyl-4-phosphonicdimorpholide (**8c**). This compound was prepared similarly to compound **8b.**

3,8-Dimethyl-1,6-diphenyl-4,9-dioxo-4,9-bis(diethylamino)-4,5,9,10-tetrahydro[1,5,2,6]-dioxadiphosphocin[3,4-d:7,8-d]dipyrazole (**9**). Compound **8b** (0.05 mol) was heated under reduced pressure (0.02 mm Hg) at 230°C for 1 hour. When the reaction mixture was cooled, an oil settled out that was triturated in benzene. The precipitate that formed was collected and recrystallized from methanol.

Tetraethyldiamino(3-methyl-5-oxo-1-phenyl-2,5-dihydropyrazol-4-yl)-chlorophosphonium chloride (**10**). To a solution of chloro ylide **3b** (0.01 mol) in acetonitrile (10 mL), a solution of hydrogen chloride (0.01 mol) in ether was added. Within 24 hours, the resulting crystalline precipitate was collected, washed with acetonitrile, and dried.

Aminodimorpholino(5-hydroxy-3-methyl-1-phenylpyrazol-4-yl)phosphonium chloride (**11c**). Into a solution of chloro ylide **3c** (0.05 mol) in methylene chloride (30 mL), cooled to 0°C, anhydrous ammonia (0.02 mol) was bubbled over 10–15 minutes, with control being exercised over the gain in weight. The precipitate of ammonium chloride was filtered off, and the filtrate was evaporated to dryness. The residual product was reprecipitated with ether from methylene chloride.

5-Hydroxy-3-methyl-1-phenylpyrazolyl-4-iminophosphonic Tetraethyldiamide (**12b**). Into a solution of chloro ylide **3b** (0.05 mol) in methylene chloride (30 mL), anhydrous ammonia (0.02 mol) was bubbled over 10–15 minutes, with control over the gain in weight. The precipitate formed was filtered off, and the filtrate was evaporated to dryness. The residue was vigorously stirred with 40% aqueous alkali (30 mL) for 5–10 minutes and then washed with water (2 × 20 mL). This was followed by extraction of the organic layer with benzene (2 × 20 mL). The benzene solution was dried over sodium sulfate and filtered. The filtrate was evaporated to dryness, and the residue was recrystallized from a mixture of methylene chloride and ether.

5-Hydroxy-3-methyl-1-phenylpyrazolyl-4-iminophosphonic Dimorpholide (**12c**). Phosphonium chloride **11c** (0.05 mol) was vigorously stirred with 40% aqueous alkali (30 mL) for 5–10 minutes, and the solid residue was then washed with water (2 × 20 mL). After extraction of the organic layer with benzene (2 × 20 mL), the resulting benzene solution was dried over sodium sulfate and filtered. The filtrate was evaporated to dryness, and the residue was recrystallized from a mixture of methylene chloride and ether.

Diethylaminotetramethyldiaminophosphonium-(3-methyl-5-oxo-1-phenyl-5H-pyrazol-4-yl)ide (**13a**). To a solution of chloro ylide **3a** (0.003 mol) in benzene (5 mL), a solution of diethylamine (0.009 mol) in benzene (5 mL) was added. The reaction mixture was refluxed for 1 hour, the resulting precipitate was filtered off, and the solvent was evaporated from the filtrate. The product was purified by reprecipitation with petroleum ether from benzene.

Anilinotetramethyldiaminophosphonium (3-Methyl-5-oxo-1-phenyl-5H-pyrazol-4-yl)ide (**14a**). To a solution of chloro ylide **3a** (0.006 mol) in benzene (7 mL), a solution of aniline (0.006 mol) in benzene (15 mL) was added. After the reaction mixture had been allowed to stand for 3 weeks, the resulting precipitate was filtered off, and the solvent was evaporated from the filtrate. The residue was washed with boiling petroleum ether (10 mL) and dried.

Dimorpholino(p-toluidino)phosphonium (3-Methyl-5-oxo-1-phenyl-5H-pyrazol-4-yl)ide (**14c**). To a solution of chloro ylide **3c** (0.002 mol) in a mixture of benzene (5 mL) and methylene chloride (10 mL), a solution of *p*-toluidine (0.002 mol) and triethylamine (0.004 mol) in methylene chloride (5 mL) was added. After the reaction mixture had been allowed to stand for 3 weeks, the reaction mixture was washed with water (2 × 30 mL). The organic layer was separated and dried over sodium sulfate, and the solvent was evaporated. The residue was recrystallized from heptane.

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