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A Representative of P,P,P-Trihalogenylides: Synthesis and Structure

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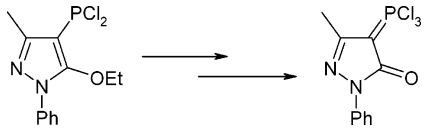

The representative of P,P,P-trichloroylides—5-methyl-2-phenyl-4-(trichlorophosphoranylidene)-2,4-dihydro-3*H*-pyrazol-3-one—was synthesized. Its constitution was confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and by X-ray analysis. Some chemical properties were studied and compared with ones of P,P,P-trimethylylide—5-methyl-2-phenyl-4-(trimethylphosphoranylidene)-2,4-dihydro-3*H*-pyrazol-3-one. DFT calculations of the model molecules were carried out.

Among the four-coordinated phosphorus trihalides of general type $Hal_3P{=}X$ (X = O, S, NR, CR_2), the key compounds in the synthesis of organophosphorus derivatives, P,P,P-trihalogenylides (X = CR_2), are mentioned only once. P-Halogenylides occupy a separate niche in P-ylide chemistry stipulated by the presence of good leaving groups. Being highly active phosphorylating agents, these compounds enter into various reactions, such as cycloaddition, heterocyclization, and others. They are very convenient objects for studying theoretical structural problems and reactivity of organophosphorus compounds. These compounds have been studied quite well, so that many references are known on P-monohalogenylides.[1] At the same time, there are only a few works devoted to P,P-dichloro-[2] and difluoro-[3] and one to trihalogenylides.[4] In P-ylides, the nature of the $P-C_{ylide}$ bond is the main point of interest and became the subject of a great number of intensive debates based on the experimental data and theoretical calculations.[5] A large number of different X-ray structures of phosphorus ylides have been determined. Despite such huge attention, the sole trichlorophosphorus ylide synthesized exists predominantly as a zwitterion and no X-ray data are available. One of the most serious hurdles in the synthesis of P-chloroylides is their propensity to 1,2-P,C-chloro shift resulting in trivalent phosphorus derivatives. Recently, starting from 4-phosphorylated-5-alkoxypyrazoles, we have synthesized P-chloro- and P,P-dichloroylides, with the final stage being vinylogous Arbuzov's reaction.[6] These compounds appeared to be quite stable, not prone to 1,2-P,C-chloro shift.

The same strategy was used for the synthesis of P,P,P-trichloroylides. The starting compound **1**, described by us earlier, is a stable and easily accessible one. Chlorination of dichlorophosphine **1** affords phosphorane **2**, moving liquid, which has in the ^{31}P NMR spectrum the sole chemical shift of −68.5 consistent with the phosphoranes. The phosphorane **2** can be stored for a few days at a temperature of 0 °C, but in solution, both in polar and nonpolar ones, it decomposes promptly. As the compound is quite labile, we fail to separate it in an analytically pure state. After numerous attempts, we have established that phosphorane **2** undergoes very selective rearrangement into the targeted trichloroylide **3** under strictly controlled conditions. The solvent of choice appeared to be methylene chloride that was thoroughly degassed and purified from any traces of chloroform. In this solvent at the temperature of 18−20 °C, the ^{31}P NMR signal of phosphorane **2** completely transforms into the signal of trichloroylide **3** (Scheme 1).

The trichloroylide **3** is a solid which crystallizes from ether. It is a quite labile compound which can be kept for a few days at room temperature. Its structure was proved by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and finally by X-ray analysis. To compare peculiarities of structures and properties of trichloroylide, P,P,P-trimethylylide **6** was synthesized. The heating of phosphonium salt **5** resulted in a mixture of the targeted ylide **6** and N-alkylated byproduct **7**. The related trimethyl-substituted ylide **6** was likewise characterized by X-ray single-crystal diffraction (Figure 1). The molecular parameters of **3** and **6** mainly correspond to those reported for semi-stabilized and stabilized phosphorus ylides: the phosphorus atom has the usual tetrahedral configuration with the shortest P−X bond located almost in the ylide plane, and the ylide carbon atom C(2) is planar. The most interesting feature of the molecular structure of ylide **3** is the noticeable shortening of the formal P=C double bond of 1.663(7) Å in comparison with all known semi-stabilized and stabilized phosphorus ylides (P=C = 1.70−1.76 Å) as well as with the corresponding value of 1.725(3) Å in the related compound **6**.[1]

DFT calculations of the model molecules (Figure 2) I (X =F), II (X = Cl), III (X =H), and IV (X = CH_3) have been carried out at the B3LYP/6-311++G(3df,3pd) level of theory to understand the nature of the shortening of the P=C double bond. Nature of the stationary points was verified by analysis of the matrices of the energy second derivatives. All calculations were performed with the Gaussian 98W program suite.[7] Electronic density distribution of obtained wave functions was interpreted in NBO method formalism.[8] Calculated data are listed in Tables 1 and 2.

The P−X3 moieties are trigonal pyramidal with one atom of the X group being located in the plane of the heterocyclic ring.

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(6) Tolmachev, A. A.; Konovets, A. I.; Kostyuk, A. N.; Chernega, A. N.; Pinchuk, A. M. *Heteroat. Chem.* **1998**, *9*, N 1, 41.

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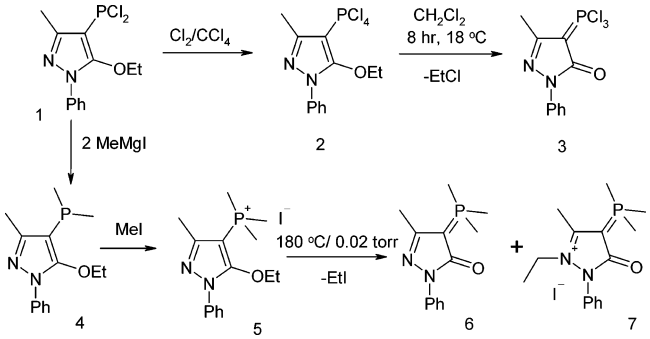
SCHEME 1



The P−C bond length significantly depends on the substituent X electronegativity (X = F, Cl, H, CH_3; P−C = 1.635, 1.662, 1.686, 1.711 Å, correspondingly). ^{13}C NMR experimental data of **3** and **6** correspond with natural charge distributions in the molecules. Thus, the greater magnetic shielding of the ylidic carbon in molecule **3**, $\delta_c = 81.2(^1J_{P-C} = 172$ Hz), as compared with that of molecule **6**, $\delta_c = 67.7(^1J_{P-C} = 126$ Hz), manifests itself in more downfield chemical shift. Moreover, the higher polarity of the P−C bond in molecule **3** confers greater value of spin−spin coupling constants $^1J_{P-C}$ as compared to the corresponding value in molecule **6**. Compared to ^{13}C NMR chemical shifts trend, ^{31}P NMR spectra have a reverse tendency.

The out-of-plane orientation of the P−X bonds with regard to the pyrazolyl ring leads to the elongation of these bonds, whereas in the in-plane orientation, this bond is the shortest one. The P−X bond lengths for the coplanar and noncoplanar bonds are X = F, Cl, H, CH_3; P−X = 1.562 and 1.565, 2.023 and 2.051, 1.090 and 1.093, 1.821 and 1.825 Å, correspondingly. Such difference is due to the strong stereoselective interaction of $n(C_{ylide})$ with σ^*(P−X). The interaction depends on the electronegativity of the substituent X and its orbitals' energy. These results are in agreement with previous experimental studies on the rotational dependence of a P−Cl bond length in a P-chloroylide.[9] Strong interactions of the lone pair of the ylidic carbon atom with π^* orbitals of the pyrazolyl moiety stabilized the molecules (Figure 2). These interactions also depend on the electronegativity of the substituents X (Table 2). The two competitive effects are responsible for the stabilization of the phosphorus ylide systems: (a) $n(C_{ylide})-\sigma^*$(P−X) interaction; (b) $n(C_{ylide})-\pi^*_{pyrazolyl}$ interaction.

Besides, some chemical properties of the ylide **3** were studied. A typical reaction of phosphorus ylides is the reaction with aldehydes (Scheme 2).

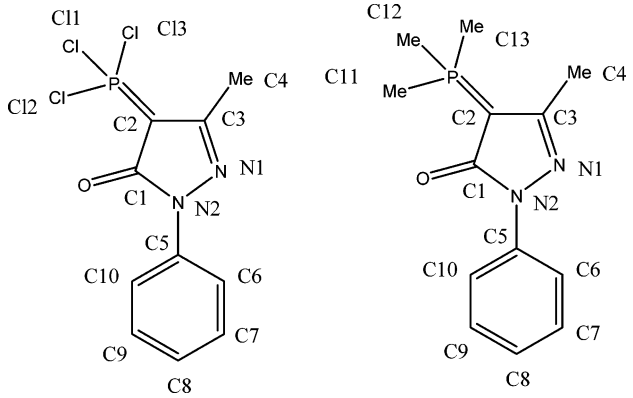


FIGURE 1. Sketches of the molecular structures of P,P,P-trichloroylide **3** and P,P,P-trimethylylide **6**. **3**: P═C(2) 1.663(7), P−Cl(1) 1.961(3), P−Cl(2) 1.978(3), P−Cl(2) 1.970(4) Å; Cl(1)−P(1)−C(2)−C(1) −171.4, Cl(2)−P(1)−C(2)−C(1) 69.6, Cl(3)−P(1)−C(2)−C(1) −50.3°; the pyrazolyl cycle N(1)N(2)C(1−3) is planar within 0.008 Å. **6**: P═C(2) 1.725(3), P−C(11) 1.778(3), P−C(12) 1.786(4), P−C(13) 1.784(3) Å; Cl(1)−P(1)−C(2)−C(1) −177.8, Cl(2)−P(1)−C(2)−C(1) −57.5, Cl(3)−P(1)−C(2)−C(1) 61.1°; the pyrazolyl cycle N(1)N(2)C-(1−3) is planar within 0.004 Å.

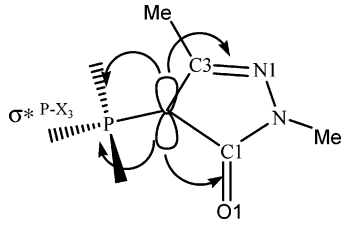


FIGURE 2. Direction of selected donor−acceptor interactions.

TABLE 1. B3LYP/6-311++G(3df,3pd) Results for Compounds I−IV

molecule	total energy (Hartree)	ZPVE correction (Hartree/particle)	lowest frequency (cm^{-1})
I	−1020.1164097	0.118803	21.5
II	−2101.1168323	0.222415	28.6
III	−722.1504039	0.147988	27.2
IV	−840.1883131	0.114239	9.7

The trichloroylide **3** reacts quite actively, but the reaction does not lead to cleavage of the P−C bond. Most probably, the reaction runs via a six-membered intermediate followed by Arbuzov rearrangement, resulting in phosphonic dichloride **8**. Both ^1H NMR (7.70 singlet) and ^{13}C NMR (92.7 singlet) spectra signals of the OCHCl moiety are singlets with typical chemical shift values. It should be noted that trimethylylide **6** reacts with aldehydes by typical Wittig reaction, affording phosphine oxide **10** and an alkene compound **9** in high yield.

The trichloroylide **3** is a thermally unstable compound which undergoes rearrangement into phosphonic dichloride **11** upon heating at 170 °C (Scheme 3). Its constitution was confirmed by a set of physicochemical methods and by the reaction with dimethylamine resulting in phosphonic diamide **12**. Trichloroylide **3** reacts with nucleophiles, as well. Thus, it reacts with methanol, yielding phosphonate **14**.

Experimental Section

5-Ethoxy-3-methyl-1-phenyl-4-(tetrachlorophosphoranyl)-1*H*-pyrazole 2. To a stirring solution of **1**, 5-ethoxy-3-methyl-1-phenylpyrazol-4-yldichlorophosphine (mp 45−46 °C, ether; 10 mmol), in

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(8) Glendening, A. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *Gaussian 98W*, revision A.7 (NBO version 3.1); Gaussian Inc.: Pittsburgh, PA, 1998.

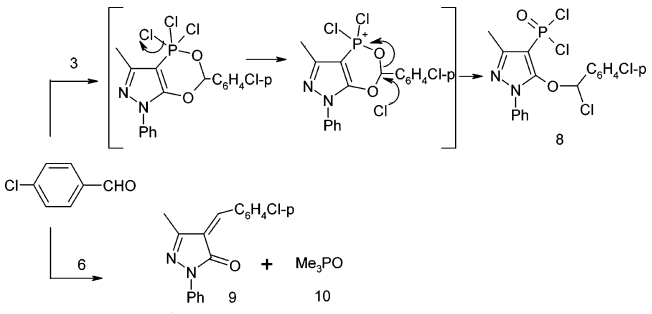
(9) Grutzmacher, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 99.

TABLE 2. Atomic Natural Charges and Energy of Interactions n(C_{ylide}) with σ^*(P−X) and $\pi^*_{pyrazolyl}$ Antibonding Orbitals[a]

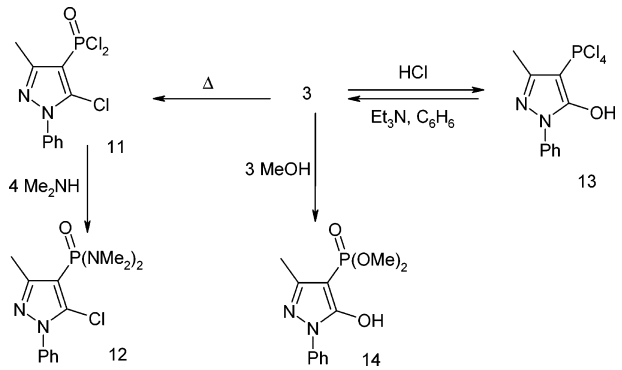
molecule	*q*(P), e	*q*(C2), e	n(C_{ylide})−σ^*(P−X) kcal/mol	n(C_{ylide})−π^*(C3−N1) kcal/mol	n(C_{ylide})−π^*(C1−O1) kcal/mol
I	2.50	−0.89	57.88	36.59	40.95
II	1.34	−0.80	63.23	53.66	67.38
III	0.92	−0.75	30.47	63.04	80.98
IV	1.56	−0.75	26.73	72.24	95.75

[a] NBO analysis shows the strong π-back-donation from the ylidic lone pair located on the carbon atom on the σ^*(P−X) orbitals (Figure 2).

SCHEME 2



SCHEME 3



carbon tetrachloride (10 mL) was added a solution of chlorine (10 mmol) in carbon tetrachloride (10 mL) during 5 min, keeping the temperature at −15(±5) °C. After 30 min, the reaction mixture was filtered to remove admixtures. The solvent was evaporated in vacuo at 0.02 Torr, keeping the temperature below 25 °C until the weight of the residue remained constant. The residue is a mobile transparent liquid. Yield 3.62 g (97%). ^{31}P NMR: δ_p = −68.5 ppm. The product decomposes on storing at 20 °C. Anal. Calcd for $C_{12}H_{13}Cl_4N_2OP$ (MW 374.04): C, 38.53; H, 3.50; Cl, 37.91; N, 7.49; P, 8.28. Found: C, 38.62; H, 3.34; Cl, 37.49; N, 7.64; P, 8.39.

5-Methyl-2-phenyl-4-(trichlorophosphoranylidene)-2,4-dihydro-3*H*-pyrazol-3-one 3. The solution of **2** (8 mmol) in dry methylene dichloride (degassed and purified from any admixtures of chloroform) was kept at the temperature of 18−20 °C for 8 h. During this time, the ^{31}P NMR signal of the tetrachlorophosphorane **2** (δ_p = −68.5) gradually disappeared, and the downfield signal of the trichloroylide **3** at δ_p = 55.9 ppm appeared, which eventually became the sole signal. The solvent was evaporated in vacuo at 0.02 Torr at a temperature lower than 40 °C and was further kept in vacuo until the residue weight remained constant. The crystalline residue was washed with dry hexane and again was kept in vacuo under the same conditions. Yield 2.23 g (90%). It can be crystallized from dry ether as yellow prisms. ^{1}H NMR (C_6D_6, 300 MHz): δ 1.93 (s, 3H), 6.95 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.26 (t, $^3J_{HH}$ = 8.7 Hz, 2H), 8.57 (d, $^3J_{HH}$ = 7.5 Hz, 2H). ^{13}C NMR (C_6D_6, 75.4 MHz): δ 16.0 (s, CH_3), 81.2 (d, $^1J_{pc}$ = 172 Hz, C), 119.1 (s, CH), 124.3 (s, CH), 129.0 (s, CH), 140.2 (s, C), 144.7 (d, $^2J_{cp}$ = 15.5 Hz, C), 164 (d, $^2J_{cp}$ = 33 Hz, C). ^{31}P NMR (C_6D_6, 121.4 MHz): δ_p 55.9. Anal. Calcd for $C_{10}H_8Cl_3N_2OP$ (MW 309.52): C, 38.81; H, 2.61; Cl, 34.36; N, 9.05; P, 10.01. Found: C, 38.64; H, 2.34; Cl, 34.69; N, 8.85; P, 9.73.

4-(Dimethylphosphino)-5-ethoxy-3-methyl-1-phenyl-1*H*-pyrazole 4. To a stirring solution of dichlorophosphine **1** (13.7 mmol) in ether (30 mL) cooled to −10 °C was added dropwise a solution of methylmagnesium iodide (30 mmol) in ether (20 mL) for 10 min. The reaction mixture was allowed to reach room temperature, then after 1 h, the reaction mixture was cooled to −10 °C and a saturated solution of aqueous NH_4Cl was added. The organic layer was separated, the solvent was evaporated, and the residue was distilled. Yield 2.58 g (81%). Mp 61−63 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.95 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 1.24 (d, $^2J_{HP}$ = 3.9 Hz, 6H), 2.44 (s, 3H), 3.77 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 6.94 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.11 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.89 (d, $^3J_{HH}$ = 7.9 Hz, 2H). ^{31}P NMR (C_6D_6, 121.4 MHz): δ_p −72.5. Anal. Calcd for $C_{14}H_{19}N_2OP$ (MW 262.29): C, 64.11; H, 7.30; N, 10.69; P, 11.81. Found: C, 63.76; H, 7.03; N, 11.04; P, 11.45.

(5-Ethoxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(trimethyl)-phosphonium iodide 5. To a solution of phosphine **4** (10 mmol) in degassed benzene (15 mL) was added a solution of methyl iodide in the benzene (15 mL). After 20 h, the precipitated solid was collected by filtration, washed with benzene (2 × 10 mL), and dried in vacuo until a constant weight was maintained. Yield 3.28 g (88%). Mp 178−179 °C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 3H), 2.48 (s, 3H), 2.59 (d, $^2J_{HP}$ = 14.3 Hz, 9H), 3.99 (q, $^3J_{HH}$ = 7.1 Hz, 2H), 7.4−7.6 (m, 5H). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ_p 10.6. Anal. Calcd for $C_{15}H_{22}IN_2OP$ (MW 404.23): C, 44.57; H, 5.49; I, 31.39; N, 6.93; P, 7.66. Found: C, 44.12; H, 5.67; I, 30.73; N, 7.34; P, 8.01. MS (API) *m*/*z* (%): 249-(100).

5-Methyl-2-phenyl-4-(trimethylphosphoranylidene)-2,4-dihydro-3*H*-pyrazol-3-one 6 and 2-Ethyl-3-methyl-5-oxo-1-phenyl-4-(trimethylphosphoranylidene)-4,5-dihydro-1*H*-pyrazol-2-ium iodide 7. Phosphonium salt **5** (0.81 g, 2 mmol) was heated in vacuo at 180 °C for 3 min with the formation of a melt. Then it was extracted with boiling benzene (4 × 10 mL). The residue was identified as compound **7**. Yield 0.29 g (30%). Mp 258−259 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.15 (t, $^3J_{HH}$ = 7.1 Hz, 3H), 2.47 (d, $^2J_{HP}$ = 14.4 Hz, 9H), 2.83 (s, 3H), 3.88 (d, $^3J_{HH}$ = 7.1 Hz, 2H), 7.31 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 7.3−7.6 (m, 3H). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ_p 13.5. Anal. Calcd for $C_{15}H_{22}IN_2OP$ (MW 404.23): C, 44.57; H, 5.49; I, 31.39; N, 6.93; P, 7.66. Found: C, 44.18; H, 5.11; I, 30.96; N, 6.61; P, 7.87.

The benzene extracts were evaporated to 20 mL and left for 2 h. The precipitated trimethylylide **6** was collected by filtration and dried. Yield 0.32 g (61%). Mp 187−188 °C; bp 200 °C (0.02 Torr). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.93 (d, $^2J_{HP}$ = 13.8 Hz, 9H), 2.23 (s, 3H), 7.06 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.34 (t, $^3J_{HH}$ =7.5 Hz, 2H), 8.01 (d, $^3J_{HH}$ = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 11.8 (d, $^1J_{pc}$ = 62 Hz, CH_3), 16.5 (s, CH_3), 67.7 (d, $^1J_{pc}$ = 126 Hz, C), 119.1 (s, CH), 123.3 (s, CH), 128.5 (s, CH), 140.3 (s, C), 147.2 (d, $^2J_{cp}$ = 11.5 Hz, C), 167.7 (d, $^2J_{cp}$ = 19.8 Hz, C). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ_p 4.8. Anal. Calcd for $C_{13}H_{17}N_2OP$ (MW 248.27): C, 62.89; H, 6.90; N, 11.28; P, 12.48. Found: C, 62.64; H, 6.71; N, 10.92; P, 12.0.

5-[Chloro(4-chlorophenyl)methoxy]-3-methyl-1-phenyl-1*H*-pyrazol-4-ylphosphonic dichloride 8. To a stirring solution of **3**

(1.5 mmol) in benzene (2 mL) at room temperature was added a solution of *p*-chlorobenzaldehyde (1.45 mmol) in benzene (1 mL). After 5 min, the solvent was evaporated in vacuo, and the residue was recrystallized from *n*-hexane. Yield 0.46 g (70%). Mp 126−127 °C (transparent prisms). ^{1}H NMR (C_6D_6, 300 MHz): δ 2.33 (s, 3H), 6.9−7.1 (m, 3H), 6.91 (d, $^3J_{HH}$ = 9 Hz, 2H), 7.21 (d, $^3J_{HH}$ = 9 Hz, 2H), 7.48 (d, $^3J_{HH}$ =7.2 Hz, 2H), 7.70 (s, 1H). ^{13}C NMR (C_6D_6, 75.4 MHz): δ 14.70 (s, CH_3), 92.7 (s, CHCl), 102.01 (d, $^1J_{pc}$ = 190.8 Hz, C), 124.64 (s, CH), 128.46 (s, CH), 128.59 (s, CH), 129.02 (s, CH), 129.15 (s, CH), 135.64 (s, C), 136.37 (s, C), 137.53 (s, C), 150.04 (d, $^2J_{cp}$ = 13 Hz, C), 152.33 (d, $^2J_{cp}$ = 32.9 Hz, C). ^{31}P NMR (C_6D_6, 121.4 MHz): δ_p 19.4. Anal. Calcd for $C_{17}H_{13}Cl_4N_2O_2P$ (MW 450.09): C, 45.37; H, 2.91; Cl, 31.51; N, 6.22; P, 6.88. Found: C, 44.92; H, 3.32; Cl, 32.01; N, 6.75; P, 7.15.

4-(4-Chlorobenzylidene)-5-methyl-2-phenyl-2,4-dihydropyrazol-3-one 9. A mixture of trimethylylide **6** (0.12 mmol) and *p*-chlorobenzaldehyde (0.12 mmol) in benzene (0.5 mL) was heated in a sealed tube at 150 °C for 10 h. The benzene was removed in vacuo. Then, the residue was heated in vacuo at 0.05 Torr at 100 °C, affording trimethylphosphineoxide. Mp 136−137 °C (0.11 mmol), 90%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.53 (d, $^2J_{HP}$ = 12.6 Hz, CH_3). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ_p 40.3. The residue was extracted with *n*-hexane (3 × 3 mL), then the hexane was evaporated to 1/3 volume. The solution was cooled to −10 °C and allowed to crystallize to the targeted product **9** as an orange powder. Yield 0.03 g (84%). Mp 101−102 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.33 (s, 3H), 7.19 (t, ^3J = 7.5 Hz, 1H), 7.26 (s, 1H), 7.35−7.5 (m, 4H), 7.39 (d, ^3J = 7.8 Hz, 2H), 8.46 (d, ^3J = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 13.4 (s, CH_3), 119.2 (s, CH), 125.1 (s, CH), 128.2 (s, C), 128.9 (s, CH), 129.2 (s, CH), 131.4 (s, C), 135.0 (s, CH), 138.4 (s, C), 139.4 (s, C), 145.2 (s, CH), 150.8 (s, C), 161.8 (s, C). Anal. Calcd for $C_{17}H_{13}ClN_2O$ (MW 296.76): C, 68.81; H, 4.42; N, 9.44. Found: C, 68.44; H, 4.03; N, 9.34. MS (API) *m*/*z* (%): (M^+ +1) (297.2, 100%), (298.4, 50%), (299.2 35%).

5-Chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-ylphosphonic dichloride 11 and P-(5-Chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-*N*,*N*,*N*′,*N*′-tetramethylphosphonic diamide 12. Trichloroylide **3** (1.13 g, 3.65 mmol) was distilled from a Claisen flask. Yield 1.0 g (88%). Colorless liquid, bp 170 °C/0.02 Torr. ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 16.9. Thus prepared dichlorophosphonate **11** (3.23 mmol) was dissolved in ether (10 mL), cooled to − 20 °C, and to the solution was added a solution of dimethylamine (1 g, 22 mmol) in ether (10 mL). The reaction mixture was allowed to reach room temperature, and after 1 h, precipitated solid was removed by filtration. The mother liquor was evaporated in vacuo. The resulting solid was recrystallized from *n*-hexane. Yield 0.55 g (52%). Mp 75−76 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.5 (s, 3H), 2.71 (d, $^3J_{HP}$ = 10.5 Hz, 12H), 7.3−7.6 (m, 5H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 14.5 (s, CH_3), 35.9 (d, $^2J_{pc}$ = 3.9 Hz, CH_3), 106.8 (d, $^1J_{pc}$ = 106.8 Hz, C), 125.4 (s, CH), 128.6 (s, CH), 128.8 (s, CH), 130.9 (d, $^2J_{cp}$ = 15.2 Hz, C), 137.6 (s, C), 154.4 (d, $^2J_{cp}$ = 10.8 Hz, C). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ_p 21.6. Anal. Calcd for $C_{14}H_{20}ClN_4OP$ (MW 326.77): C, 51.46; H, 6.17; Cl, 10.85; N, 17.15; P, 9.48. Found: C, 51.11; H, 6.55; Cl, 11.04; N, 17.02; P, 9.79. MS (API) *m*/*z* (%): (M^+ + 1) 327 (100).

3-Methyl-1-phenyl-4-(tetrachlorophosphoranyl)-1*H*-pyrazol-5-ol 13. To a stirring solution of **3** (1.45 mmol) in benzene (10 mL) cooled with an ice bath was added dropwise an ethereal solution of hydrogen chloride (3 mL, 0.5 N). After 4 h, the precipitated solid was collected by filtration, washed with benzene (2 × 5 mL), and dried in vacuo at 50−60 °C. Yield 0.38 g (76%). Mp 124−125 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.73 (s, 3H), 7.28 (t, $^3J_{HH}$ = 10.5 Hz, 1H), 7.46 (t, $^3J_{HH}$ = 10.5 Hz, 2H), 7.84 (d, $^3J_{HH}$ =7.8 Hz, 2H), 13.05 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 14.6 (s, CH_3), 84.2 (d, $^1J_{pc}$ = 191.8 Hz, C), 120.9 (s, CH), 126.6 (s, CH), 129.0 (s, CH), 135.6 (s, C), 148.1 (d, $^2J_{cp}$ = 21.6 Hz, C), 160.5 (d, $^2J_{cp}$ = 27.5 Hz, C). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ_p 69.2. On addition of triethylamine in an NMR tube, the signal δ_p 69.2 disappeared and the sole signal δ_p 55.7 of trichloroylide **3** formed. Anal. Calcd for $C_{10}H_9Cl_4N_2OP$ (MW 345.98): C, 34.72; H, 2.62; Cl, 40.99; N, 8.10; P, 8.95. Found: C, 34.33; H, 3.02; Cl, 41.52; N, 8.53; P, 9.33.

Dimethyl 5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-ylphosphonate 14. To a solution of trichloroylide **3** (0.82 g, 2.65 mmol) in benzene (10 mL) was added a mixture of methanol (8 mmol) and triethylamine (8.6 mmol) in benzene (10 mL) at 0 °C with stirring. The reaction mixture was allowed to reach room temperature, and after 1 h, the precipitated solid was removed by filtration. The mother liquor was evaporated; the residue was dissolved in ether (10 mL) and cooled to −15 °C. The precipitated oil was separated and dried in vacuo. Yield 0.44 g (60%). Upon distillation, the product decomposes. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.24 (s, 3H), 3.41 (d, $^3J_{HP}$ = 11.7 Hz, 6H), 6.9 (t, $^3J_{HH}$ = 6.9 Hz, 1H), 7.4 (t, $^3J_{HH}$ = 8.1 Hz, 2H), 7.73 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 10.27 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 13.8 (s, CH_3), 52.7 (d, $^2J_{pc}$ = 4.0 Hz, CH_3), 82.4 (d, $^1J_{pc}$ = 219.0 Hz, C), 121.3 (s, CH), 126.6 (s, CH), 137.6 (s, C), 149.4 (d, $^2J_{cp}$ = 9.6 Hz, C), 159.6 (d, $^2J_{cp}$ = 21.9 Hz, C). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ_p 24.6. Anal. Calcd for $C_{12}H_{15}N_2O_4P$ (MW 282.24): C, 51.07; H, 5.36; N, 9.93; P, 10.97. Found: C, 51.44; H, 5.75; N, 9.41; P, 11.44. MS (API) *m*/*z* (%): (M^+ + 1) 283 (100).

Supporting Information Available: CIF files of both ylides **3** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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