Synthetic Communications®, 39: 1626–1639, 2009
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ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910802564733

Reactions of Trisdialkylaminophosphines with Acrylohydrazide and Imidazolinone Derivatives for the Synthesis of New Organophosphorus Derivatives

Mona H. N. Arsanious
Department of Organometallic and Organometalloid Chemistry, National Research Center, Dokki, Cairo, Egypt

Abstract: Trisdimethylaminophosphine reacts with 2-benzamido-*N*-arylidene-3-aryl-acrylohydrazide to give phosphoryl benzamide and phosphoryl-cyano-benzamide adducts depending on the reaction conditions. Moreover, 1-aryliden-amino-2-phenyl-4-aryliden-2-imidazolin-5-ones react with trisdialkylaminophosphines to yield tetraalkylphosphonic diamide adducts. Possible reaction mechanisms are considered, and the structural assignments are based on analytical and spectroscopic evidence and X-ray analysis.

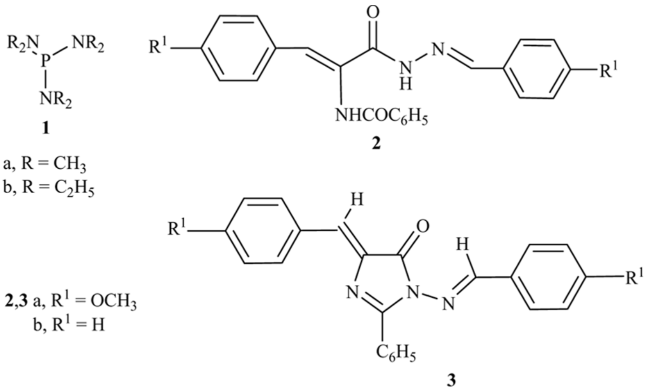
Keywords: 3-Arylacrylohydrazides, 4-aryliden-2-imidazolin-5-ones, trisdialkylaminophosphines

INTRODUCTION

Hydrazides and heterocyclic ring systems represent important classes of compounds not only for their theoretical interest but also for their biological activities.[1–3] Furthermore, it is known that phosphorus substituents regulate important biological functions[4–6] and that the incorporation of phosphorus into organic molecules could increase their biological and pharmaceutical activity.[7–9] This together with our interest

Received October 5, 2008.

Address correspondence to Mona H. N. Arsanious, Department of Organometallic and Organometalloid Chemistry, National Research Center, Dokki, Cairo, Egypt. E-mail: mona.arsanious@gmail.com



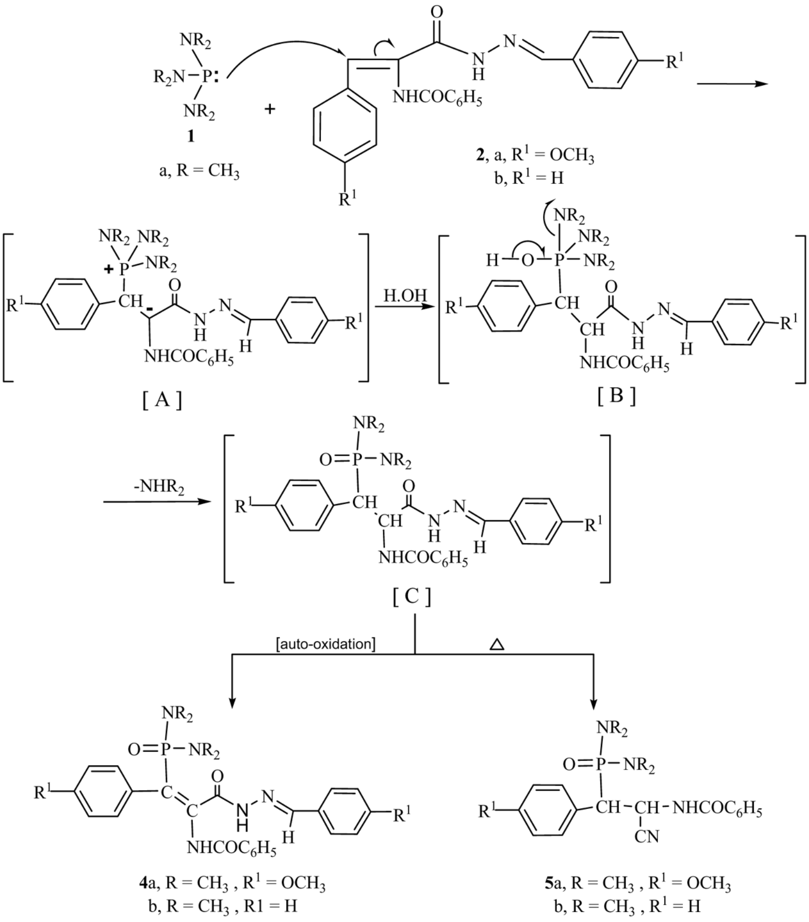
Scheme 1. Reagents and substrates.

in organophosphorus chemistry[10–12] led us to explore the synthesis of new phosphorus compounds that may possess increased biological activity. The present study deals with the reaction of trisdialkylaminophosphines **1a** and **1b** with 2-benzamido-*N*-arylidene-3-aryl-acrylo-hydrazides **2a** and **2b** and its cyclic-dehydration derivatives namely 1-aryliden-amino-2-phenyl-4-arylidene-2-imidazolin-5-one **3a** and **3b** (Scheme 1).

RESULTS AND DISCUSSION

When 2-benzamido-*N*-(4-methoxy-benzylidene)-3-(4-methoxyphenyl) acrylohydrazide (**2a**) was allowed to react with two mol. equivalents of trisdimethylaminophosphine (**1a**) in boiling toluene for 10 h, two adducts were formed as compounds **4a** (major product) and **5a** (Scheme 2).

Structural support for *N*-[(Z)-2-{bis(dimethylamino)phosphoryl-1-[(2-methoxyphenyl)methylidene)hydrazine)carbonyl]-2-[(4-methoxyphenyl) ethenyl]benzamide (**4a**) is deduced from its spectroscopic data. The infrared (IR) spectrum of **4a**, in KBr, revealed the presence of an intense band at 1251 cm^{-1} (P=O) absorption[13] and two bands at 1320, 838 cm^{-1} due to the absorption of $P[N(CH_3)_2]_2$,[14] 1692 cm^{-1} (C=O), and 3100 (NH). The ^1H NMR spectrum of **4a** ($CDCl_3$, δ ppm) gives a doublet at $\delta = 2.73$ ppm with $^2J_{HP} = 10.8$ Hz due to 12 protons of the two equivalent NMe_2 groups attached to the phosphorus atom, one singlet at 7.58 (N=CH), and two singlets at 8.84 and 9.88 ppm (NH). The ^{13}C NMR spectrum of **4a** adds good support to the proposed structure, which reveals two signals at 165.9 and 165.6 (2 C=O) and two doublets of ethenyl C=C attached to the phosphorus atom at 110.3 ($^1J_{CP} = 141.7$ Hz) and



Scheme 2. Mechanism for the formation of adducts **4** and **5**.

128.7 ($^{2}J_{CP} = 38.4$ Hz) ppm.[15] Moreover, the structure assigned to **4a** was unambiguously supported by X-ray analysis (Fig. 1, Table 1).

Carrying out the reaction of **2a** with two mol equivalents of **1a** in boiling xylene for 3 h led to formation of **4a** and **5a** (major product) (Scheme 2). Structure elucidation of compound **5a** is based on its spectroscopic data (cf. Experimental). The ^{1}H NMR of **5a** reveals signals at $\delta = 2.85$ [d, 12H, $^{3}J_{HP} = 9.6$ Hz, 2 N-$(CH_3)_2$], 5.31 (dd, 1H, $^{2}J_{HP} = 24.6$, $J_{HH} = 10.5$ Hz), 3.74 (dd, 1H, $^{3}J_{HP} = 11.2$ Hz, $J_{HH} = 10.5$ Hz) for methane attached to phosphorus. The ^{31}P NMR shows signal $\delta = 33.2$ ppm. The mass spectrum of **5a** yielded a prominent ion peak for M^{+} at m/z 414.

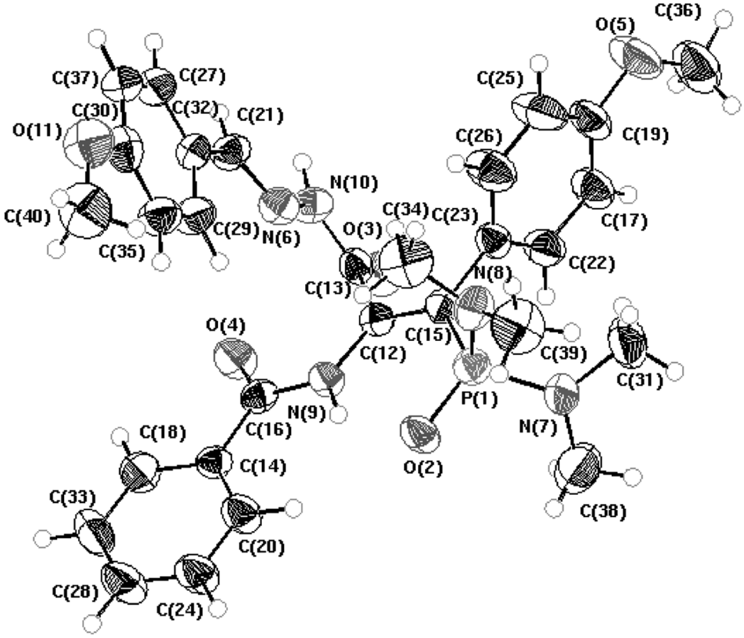


Figure 1. Compound **4a**: Selected bond lengths (Å) and angles (°): P1–O2 1.486 (2), P1–N7 1.640 (2), P1–N8 1.632 (2), P1–C15 1.804 (2), N7–C31 1.454 (4), N7–C38 1.465 (4), N8–C34 1.457 (4), N8–C39 1.466 (4), C15–C12 1.353 (3), O2–P1–N7 110.47 (11), O2–P1–N8 116.92 (11), O2–P1–C15 109.36 (10), N7–P1–C15 111.48 (11), N8–P1–C15 104.59 (11), N8–P1–N7–C31 −48.2 (4), N7–P1–N8–C34 169.0 (4), N8–P1–N7–C38 154.3 (4), N7–P1–N8–C39 −34.2 (4).

The structure of compound **5a** is confirmed by X-ray analysis instead of the expected imidazolone adduct **6** (cf. Fig. 2, Table 1, Scheme 3).

Similarly, **2b** reacts with two mol. equivalents of trisdimethylaminophosphine (**1a**) in boiling toluene to give colorless crystalline compounds formulated as **4b** (major product) and **5b**, whereas the reaction of **2b** with two mol. equivalents of **1a** in boiling xylene gives **4b** and **5b** (major product) (Scheme 2).

The structure of new compounds **4b** and **5b** are assigned on the basis of their full set of spectral data (cf. Experimental).

It is worth mentioning that when **2a** and **2b** were allowed to react with trisdimethylaminophosphine **1a** using 1:1 mol. equivalents, a mixture of the substrates and products **4a,b** and **5a,b** were obtained, whereas when using two mol. equivalents of **1a**, adducts were obtained as sole products.

A possible explanation for the reaction of trisdiameylaminophosphines **1a** with **2a,b** is shown in Scheme 2. Initial attack of

Table 1. Crystal structure and data refinement parameters

Compound	**4a**	**5a**
Empirical formula	$C_{29}H_{34}N_5PO_5$	$C_{21}H_{27}N_4O_3P$
Formula weight	563.595	414.446
Crystal system/space group	Monoclinic	Prismatic
a (Å)	11.3248 (4)	9.1887 (7)
b (Å)	16.7066 (6)	10.6982 (8)
c (Å)	18.2159 (8)	13.2843 (14)
α (°)	90.00	98.851
β (°)	12. (18) $\times 10^{10}$	104.953
γ (°)	90.00	114.654
V ($Å^3$)	2960.7 (2)	1094.6 (2)
Z	4	2
Dx (Mg/cm^{-3})	1.264	1.257
μ (mm^{-1})	0.14	0.15
Color/shape	Colorless/cube	Colorless/prismatic
Temperature (K)	298	298
Theta range for collection	2.910–21.967	2.910–22.986
Reflections collected	6648	4888
Independent reflections	3948	3387
Data/restraints/parameters	262	356
R (gt)	0.060	0.053
Final R indices [$I > 2\sigma(I)$]	R_{int} 0.035	R_{int} 0.049

aminophosphine **1a** on the most reactive center of the α,β-unsaturated carbonyl system leads to the formation of the dipolar adduct [**A**]. Addition of elements of water (unavoidable moisture) to intermediate [**A**] produces a transient intermediate [**B**] with pentacovalent phosphorus.[8] Adducts **4a,b** are then formed by loss of $HNMe_2$ molecule followed by auto-oxidation[16] of an intermediate such as [**C**] (Scheme 2).

Formation of products **5a** and **5b** can be explained in terms of fission of the hydrazide bond of intermediate [**C**] followed by formation of the corresponding cyanide by the action of excess of trisdialkylaminophoshine **1**.[17,18] The isolation of diarylideneazine confirms this postulation (Scheme 3).

We have also investigated the reaction of trisdialkylaminophosphine **1a,b** with 1-arylidenamino-2-phenyl-4-aryliden-2-imidazolin-5-ones **3a,b** to establish whether they would behave in a similar manner. Thus, we have found that the reaction of **1a** and/or **1b** with **3a** and/or **3b** in tetrahydrofuran (THF) and/or toluene proceeds at room temperature to give chromatographically pure adducts formulated as tetraalkylphosphonic diamides **7a–d** (Scheme 4). The structural assignments for **7a–d** were deduced from their elemental analyses; infrared (IR); ^1H, ^{13}C, and ^{31}P NMR, and mass spectral data (cf. Experimental).

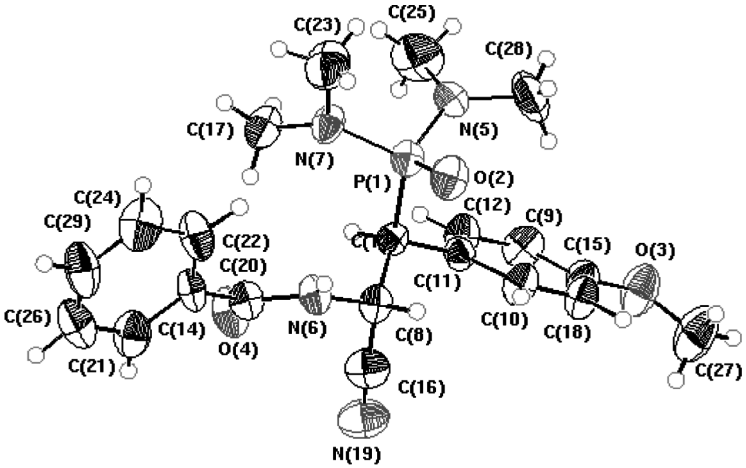
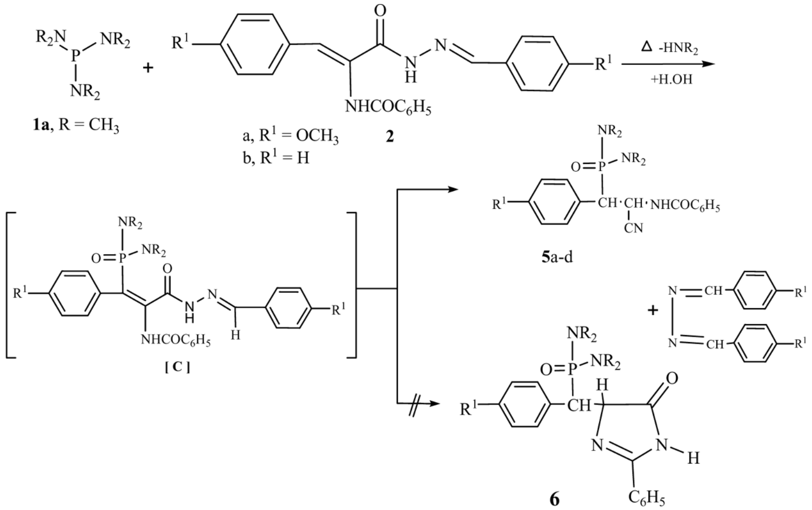
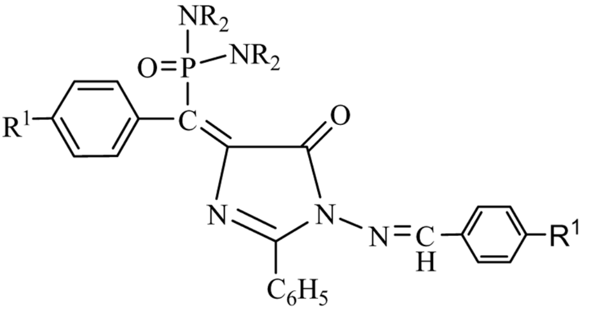


Figure 2. Compound **5a**: Selected bond lengths (Å) and angles (°): P1–O2 1.483 (2), P1–N5 1.642 (3), P1–N7 1.641 (3), P1–C13 1.826 (4), N5–C25 1.434 (5), N5–C28 1.469 (5), N7–C17 1.458 (5), N7–C23 1.442 (5), C13–C11 1.519 (5), C16–N19 1.132 (5), O2–P1–N7 113.9(2), O2–P1–N5 110.1 (2), O2–P1–C13 108.76 (15), N7–P1–C13 107.9 (2), N5–P1–N7 106.7 (2), N5–P1–C13 109.4 (2), N5–P1–N7–C23 −71.3 (6), N5–P1–N7–C17 87.1 (6), N7–P1–N5–C25 −40.1 (6), N7–P1–N5–C28 154.1 (7).



Scheme 3. Formation of adduct **5** not **6**.



7a, R = CH_3 , R^1 = OCH_3
b, R = C_2H_5 , R^1 = OCH_3
c, R = CH_3 , R^1 = H
d, R = C_2H_5 , R^1 = H

Scheme 4.

From the results of the present investigation, it could be concluded that the reaction of trisdimethylaminophosphines **1a** with arylacrylohydrazides **2** leads to different products depending on the reactions conditions. Arylideneimid-azolinones **3** react with trisdialkylaminophosphines **1a,b** at room temperature to give tetraalkylphosphonic diamides. Besides, the addition of the phosphorus reagents occurs at the unsaturated carbon atom β- to the carbonyl group of substrates **2** and **3** respectively to give the new substituted dialkylamino-phosphoryl derivatives.

EXPERIMENTAL

Melting points were determined in open glass capillaries using an Electrothemal IA 9000 series digital melting-point apparatus (Electrothermal, Essex, U.K.) and are uncorrected. 2-Benzamido-N-arylidene-3-aryl-acrylhydrazides **2a,b** and 1-arylidenamino-2-phenyl-4-aryliden-2-imidazolin-5-ones **3a,b** were prepared according to reported procedures.[19] The IR spectra were measured in KBr pellets with a Perkin-Elmer Infracord spectrophotometer model 157 (Grating). The ^1H and ^{13}CNMR spectra were recorded in $CDCl_3$ and dimethyl sulfoxide (DMSO) as solvent on a Joel 300 MHz spectrometer, and the chemical shifts were recorded in δ values relative to tetramethylsilane (TMS). The ^{31}P NMR spectra were taken with a Varian CFT-20 (vs. external 85% H_3PO_4 standard). The mass spectra were performed at 70 eV on a Shimadzu GCS-OP 1000 Ex spectrometer provided with a data system. Elemental analyses were performed using the Elmeuter Varu EL (Germany) instrument.

Reaction of 2-Benzamido-N-(4-methoxybenzylidene)-3-(4-methoxyphenyl) acrylohydrazide (2a) with Trisdimethylaminophosphine 1a

Trisdiamethylaminophosphine **1a** (2 mmol) was added dropwise to a solution of compound **2a** (0.42 g, 1 mmol) in toluene (30 cm^3), and the reaction mixture was refluxed for 10–12 h. After evaporation of the volatile materials under reduced pressure, the residue was applied to silica-gel column chromatography. The eluent, yield, and mp are given for adducts **4a** and **5a**.

N-2-[Bis(dimethylamino) phosphoryl]-1-[(2-(4-methoxyphenyl) methylidene) hydrazino)carbonyl]-2-[(4-methoxyphenyl)ethenyl]benzamide (4a)

Eluent: ethyl acetate/petroleum ether (65:35, v/v). Product **4a** was separated as colorless crystals, Yield 60%, mp 247–248°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.73{d, 12H, $^3J_{HP} = 10.8$ Hz, P-[N(CH_3)$_2$]$_2$}, 3.74, 3.81 [2s, 6H, 2 (OCH_3)], 6.82–6.86 (d, 2H, $J = 8.1$ Hz, Ar), 6.98–7.01 (d, 2H, $J = 8.1$ Hz, Ar), 7.45–7.48 (m, 5H, Ar), 7.82–7.85 (d, 2H, $J = 8.1$ Hz, Ar), 7.58 (s, 1H, =C*H*), 8.02–8.05 (d, 2H, $J = 8.1$ Hz, Ar), 8.84, 9.88 (2s, 2H, 2NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 110.3 (d, $^1J_{CP} = 141.7$ Hz, C=*C*-P), 128.7 (d, $^2J_{CP} = 38.4$ Hz, *C*=C-P), 36.1{d, $^2J_{CP} = 27$ Hz, P[N-(*C*H_3)$_2$]}, 54.8, 54.5 (p-O*C*H_3), 160.4, 113.0, 130.2, 126.4 (*C*$_6H_4$), 128.2, 126.2, 113.4, 158.5 (*C*$_6H_4$), 165.9, 165.6 (2*C*=O), 144.6 (*C*=N-N), 131.6, 128.1, 127.4, 126.0 (*C*$_6H_5$); IR (KBr): ν_{max}/cm^{-1} 1692 (CONH), 3100 (NHCOPh), 1251 (P=O), 1320, 860 [$N(CH_3)_2$]. MS m/z (%) 563 (M^+, 45). For $C_{29}H_{34}N_5O_5P$ (563.58) calcd.: C, 61.80; H, 6.08; N, 12.43; P, 5.50%. Found: C, 61.86; H, 6.20; N, 12.36; P, 5.60%.

X-Ray Crystallographic Study[20–24]

A single crystal of **4a** was grown by crystallization from cyclohexane. The crystal structure was solved and refined, using maXus (Nonius, Delft, and Mac Science, Japan). Mok$_\alpha$ ($\lambda = 0.71073$ Å) and a graphite monochromator were used for data collection. A summary of the crystal analysis parameters is given in Table 1. CCDC 698572 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

N-[2-[Bis(dimethylamino)phosphoryl]-1-cyano-2-(4-methoxyphenyl)ethyl]benzamide (5a)

Eluent: acetone/petroleum ether (30:70, v/v). Product **5a** was separated as colorless crystals. Yield 20%; mp 226–227°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.85 [d, 12H, $^3J_{HP} = 9.6$ Hz, $P(N\text{-}(CH_3)_2)_2$], 3.74 (dd, 1H, $^3J_{HP} = 11.2$ Hz, $J_{HH} = 10.5$ Hz, C*H*-C*H*-P), 3.77 (s, 3H, p-OC*H*$_3$), 5.31 (dd, 1H, $^2J_{HP} = 24.6$ Hz, $J_{HH} = 10.5$ Hz, C*H*-C*H*-P), 6.85 (d, 1H, $J = 7.8$ Hz, Hz, Ar), 7.44–7.55 (m, 7H, Ar),7.95 (d, 1H, $J = 7.8$ Hz, Ar), 9.49 (s, 1H, N*H*). IR (KBr): v_{max}/cm^{-1} 1240 (P=O), 1713 (C=O), 3100 (NH); MS m/z (%) 414 (M^+, 100). For $C_{21}H_{27}N_4O_3P$ (414.45) calcd.: C, 60.86; H, 6.57; N, 13.2; P, 7.47%. Found: C, 60.94; H, 6.76; N, 13.05; P, 7.54%.

X-Ray Crystallographic Study[20–24]

A single crystal of **5a** was grown by crystallization from n-hexane. The crystal structure was solved and refined using maXus (Nonius, Delft, and Mac Science, Japan). Mok$_\alpha$ ($\lambda = 0.71073$ Å) and a graphite monochromator were used for data collection. A summary of the crystal analysis parameters is given in Table 1. CCDC 698573 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reaction of 2-(Benzamido)-N-benzylidene-3-phenylacrylohydrazide (2b) with Trisdmethylaminophosphine 1a

To a solution of **2b** (0.36 g, 1 mmol) in 30 cm^3 toluene, trisdimethylaminophosphine **1a** (2 mmol) was added dropwise at room temperature with stirring, and the reaction mixture was refluxed for 6–8 h. The reaction mixture was evaporated under reduced pressure, and the residue was applied to silica-gel column chromatography. The eluent, yield, and mp are given for adducts **4b** and **5b**.

N-2-[Bis(dimethylamino)phosphoryl]-1-[(2-(phenylmethyliden)hydrazino) carbonyl]-2-[(4-methoxyphenyl)ethenyl]benzamide (4b)

Eluent: ethyl acetate/petroleum ether (60:40, v/v). Product **4b** was separated as colorless crystals. Yield 55%; mp 271–272°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.83 [d, 12H, $^3J_{HP} = 8.1$ Hz, $P(N(CH_3)_2)_2$], 7.91 (s, 1H, N=C*H*), 7.28–7.24 (m, 10H, Ar), 7.51–7.46 (m, 5H, Ar), 9.55 (b, 2H, 2N*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 113.2 (d, $^1J_{CP}$ = 141.2 Hz, C=*C*-P), 128.2 (d, $^2J_{CP}$ = 38.1 Hz, *C*=C-P), 35.71{d, $^2J_{CP}$ = 28.3 Hz, P[N (*C*H_3)$_2$]$_2$}, 143.0 (N=*C*H), 168.0, 163.6 (2*C*=O). IR (KBr): v_{max}/cm^{-1} 1230 (P=O), 1692 (C=O); MS m/z (%) 503 (M^+, 20). For $C_{27}H_{30}N_5O_3P$ (503.40) calcd. C, 64.40; H, 6.01; N, 13.91; P, 6.15. Found: C, 64.0; H, 6.12; N, 13.79; P, 6.10%.

N-[2-[Bis(dimethylamino)phosphoryl]-1-cyano-2-(phenyl)ethyl]benzamide (5b)

Eluent: ethyl acetate/petroleum ether (60:40, v/v). Product **5b** was separated as colorless crystals. Yield 20%; mp 243–245°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.37 [d, 12H, $^3J_{HP}$ = 9.2 Hz, P(N-(C*H*$_3$)$_2$)$_2$], 3.79 (dd, 1H,$^3J_{HP}$ = 14.5 Hz, J_{HH} = 9.9 Hz, C*H*-C*H*-P), 5.32 (dd, 1H, $^2J_{HP}$ = 22.1 Hz, J_{HH} = 9.9 Hz, C*H*-C*H*-P), 7.48–7.30 (m, 3H, Ar),7.55–7.53 (m, 5H, Ar), 7.95–7.93 (d, 2H, Ar), 9.59 (s, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 43.1 (d,$^1J_{CP}$ = 136.25 Hz, H*C*-P), 44.1 (d, $^2J_{CP}$ = 24.0 Hz, *C*H-CH-P), 36.4 {d, $^2J_{CP}$ = 22.6 Hz, P[N-(*C*H_3)$_2$]}, 116.4 (*C*N), 166.4 (*C*=O), 132.1, 128.7, 127.3, 130 (C_6H_5); ^{31}P NMR (300 MHz, δ (ppm): 33.5. IR (KBr): v_{max}/cm^{-1} 1240 (P=O), 1715 (C=O), 3200 (NH); MS m/z (%) 384 (M^+, 100). For $C_{20}H_{25}N_4O_2P$ (384.41) calcd.: C, 62.49; H, 6.56; N, 14.57; P, 8.06%. Found: C, 62.56; H, 6.49; N, 14.50; P, 8.16%.

Reaction of Trisdimethylaminophosphine 1a with 2a and/or 2b

To a solution of **2a** and/or **2b** (1 mmol) in 30 cm^3 xylene, trisdialkylaminophosphine **1a** (2 mmol) was added dropwise, and the reaction mixture was refluxed for 3 h. After evaporation of the volatile materials under reduced pressure, the residue was applied to silica-gel column chromatography to give **4a,b** and **5a,b**. Compounds **4** and **5** were obtained in refluxing toluene in yields of 20% and 60%, respectively.

Reaction of 4-(4-Methoxybenzylidene)-1-(4-methoxybenzylideneamino)-2-phenyl-1H-imidazol-5(4H)-one 3a with Ttrisdialkylaminophosphines 1a,b

To a solution of **3a** (0.41 g, 1 mmol) in THF (20 cm^3), **1a** and/or **1b** (2 mmol) was added dropwise, and the reaction mixture was stirred for

15–20 h at room temperature. The reaction mixture was evaporated under reduced pressure, and the residue was applied to silica-gel column chromatography. The eluent, yield, and mp are given for adducts **7a** and **7b**.

N,N,N,N-Tetramethyl-P-{1-[(4-methoxyphenyl)methylidene]amino-[(5-oxo-2-phenyl-4,5-dihydro-1H-imidazol-4-ylidene)(4-methoxyphenyl) methyl]phosphonic diamide (7a)

Eluent: acetone/petroleum ether (25:75, v/v). Product **7a** was separated as colorless crystals. Yield 60%; mp 223–225°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.75 (d, 12H, $^{3}J_{HP} = 9.9$ Hz, P(N-CH_3)$_2$), 3.76, 3.83 (2s, 6H, 2OCH_3), 6.88–6.85 (m, 4 H, Ar), 7.49–7.37 (m, 5H, Ar), 8.08–8.05 (m, 4H, Ar), 7.58 (s, 1H, =C*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 132.0 (C=*C*-P, d, $^{1}J_{CP} = 124.6$ Hz), 135.8 [d, $^{2}J_{CP} = 28.7$ Hz, P-C=*C*], 42.5 {d, $^{2}J_{CP} = 26.7$ Hz, P[N(CH_3)$_2$]$_2$}, 169.6 (*C*=O), 164.1 (N =*C*-imidazolone), 154.8, 113.0, 126.1, 132.2 (C_6H_4), 158.6, 114.2, 127.6, 128.5 (C_6H_4), 132.1, 128.7, 127.3,130.4 (C_6H_5); ^{31}P NMR (300 MHz) δ (ppm): 34.5; IR (KBr) v_{max}/cm^{-1}1240 (P=O),1312, 865 {P[N(Me)$_2$]$_2$}; MS m/z (%) 545 (M^+, 35). For $C_{29}H_{32}N_5O_4P$ (545.57) calcd.: C, 63.84; H, 5.91; N, 12.84; P, 5.68%. Found: C, 63.95; H, 5.81; N, 12.70; P, 5.7%.

N,N,N,N-Tetraethyl-P-{1-[(4-methoxy-phenyl)methylidene]amino-[(5-oxo-2-phenyl-4,5-dihydro-1H-imidazol-4-ylidene) (4-methoxyphenyl)methyl]phosphonic diamide}(7b)

Eluent: ethyl acetate/petroleum ether (40:60, v/v). Product **7b** was separated as colorless crystals. Yield 70%, mp 233–235°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.06 [t, 12H, N-(CH_2C*H_3*)$_2$], 3.87, 3.85 (2s, 6H, 2OCH_3), 3.35 [q, 8H, N(CH_2CH_3)$_2$], 6.82–6.91(m, 2H, Ar), 6.94 (d, 1H, $J = 8.7$ Hz, Ar), 7.45–7.47 (m, 5H, Ar), 7.59–7.67 (m, 4H, Ar), 8.40 (d, 1H, $J = 8.7$ Hz, Ar), 7.56 (s, 1H, =C*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 132.7 (d, $^{1}J_{CP} = 130.2$ Hz, C=*C*-P), 136.1 (d, $^{2}J_{CP} = 32.2$ Hz, *C*=C-P), 168.2 (*C*=O), 165.6 (N=*C*), 40.6 [N(*C*H_2CH_3)$_2$], 14.8 {d, $^{2}J_{CP} = 22.4$ Hz, P[N(CH_2-*C*H_3)$_2$]}, 56.8, 54.8 (p-O*C*H_3), 162.8, 113.0, 132.2, 126.0 (C_6H_4), 158.6, 114.2, 127.4, 128.1 (C_6H_4), 129.3, 127.5, 126.8, 131.3 (C_6H_5). IR (KBr): v_{max}/cm^{-1} 1240 (P=O) cm^{-1}, 1310, 854 {P[N(Et)$_2$]$_2$}. MS m/z (%) 601 (M^+, 12). For $C_{33}H_{40}N_5O_4P$ (601.68) calcd. C, 65.87; H, 6.70; N, 11.64; P, 5.15%. Found: C, 65.90; H, 6.86; N, 11.58; P, 5.20%.

Reaction of 4-(Benzylidene)-1-(benzylideneamino)-2-phenyl-1H-imidazol-5(4H)-one (3b) with Trisdialkylaminophosphines 1a,b

To a solution of **3b** (0.35 g, 1 mmol) in toluene (20 cm^3), **1a** and/or **1b** (2 mmol) were added dropwise, and the reaction mixture was stirred for 15–20 h at room temperature. The reaction mixture was evaporated under reduced pressure, and the residue was applied to silica-gel column chromatography. The eluent, yield, and mp are given for adducts **7c** and **7d**.

N,N,N,N-Tetramethyl-P-{1-[(5-oxo-2-phenyl-1-[(phenymethylidene)-amino]-4,5-dihydro-1 H-imidazol-4-ylidene)(phenyl)methyl]phosphonic diamide (7c)

Eluent: acetone/petroleum ether (30:70, v/v). Product **7c** was separated as colorless crystals, (0.34 g, 72%). mp: 223°C. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.73 [d, 12 H, $^3J_{HP} = 10.8$ Hz, $P(N(CH_3)_2)_2$], 7.91 (s, 1H, N=C*H*), 7.32–7.24 (m, 10H, Ar), 7.52–7.4 (m, 5H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 134.2 (d, $^1J_{CP} = 135.2$ Hz, C=*C*-P), 129.8 (d, $^2J_{CP} = 28.1$ Hz, *C*=C-P), 35.7 {d, $^2J_{CP} = 22.3$ Hz, $P[N(CH_3)_2]_2$}, 143.0 (N=*C*H), 168.0 (*C*=O), 126.2, 129.5, 129.2, 126.0 (C_6H_5), 128.6, 124.2, 127.4, 128.1 (C_6H_5), 129.3, 127.5, 126.8, 127.3 (C_6H_5). ^{31}P NMR (300 MHz, $CDCl_3$) δ (ppm): 33.2. IR (KBr): v_{max}/cm^{-1} 1240 (P=O), 1320, 860 {$P[N\text{-}(Me)_2]_2$}; MS m/z (%) 485 (M^+, 14). For $C_{27}H_{28}N_5O_2P$ (485.52) calcd.: C, 66.79; H, 5.81; N, 14.42; P, 6.3. Found: C, 66.88; H, 5.72; N, 14.32; P, 6.28%.

N,N,N,N-Tetraethyl-P-{1-[(5-oxo-2-phenyl-1-[(phenymethylidene) amino]-4,5-dihydro-1H-imidazol-4-ylidene)(phenyl)methyl]phosphonic} diamide 7d

Eluent: acetone/petroleum ether (20:80, v/v). Product **7d** was separated as colorless crystals. Yield 70%, mp 214–215°C; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.93 [t, 12H, $N(CH_2CH_3)_2$], 3.87, 3.85 (2s 6H, $2OCH_3$), 4.24 [q, 8H, $N(CH_2CH_3)_2$], 7.45–7.47 (m, 5H, Ar), 7.59–7.67 (m, 10H, Ar),7.56 (s, 1H, =C*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 132.7 (d, $^1J_{CP} = 140.4$ Hz, C=*C*-P), 131.1 (d, $^2J_{CP} = 36.8$ Hz, *C*=C-P), 40.8 [$N(CH_2.CH_3)_2$], 14.6 {d, $^2J_{CP} = 20.6$ Hz, $P[N(CH_2CH_3)_2]$, 126.8, 131.0, 132.2, 126.0 (C_6H_5), 128.6, 124.2, 127.4, 128.1 (C_6H_5), 129.3, 127.5, 126.8, 131.3 (C_6H_5). IR (KBr) v_{max}/cm^{-1} 1240 (P=O), 1315, 850 {$P[N(Et)_2]_2$. MS m/z (%) 541 (M^+, 20). For $C_{31}H_{36}N_5O_2P$ (541.62) calcd.: C, 68.74; H, 6.70; N, 12.93; P, 5.72. Found: C, 68.92; H, 6.82; N, 12.80; P, 5.60%.

ACKNOWLEDGMENT

We thank Prof. Dr. Ibrahim S. A. Farag, Departement of Solid State Physics, National Research Center, Dokki, Cairo, Egypt, and his coworker for doing X-ray diffraction analysis.

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