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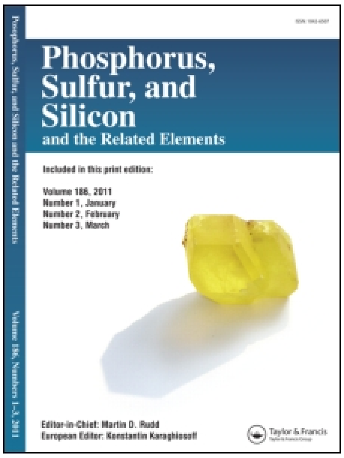

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Organophosphorus Chemistry 34 1 . The Reaction of Alkyl Phosphites and Hexamethylphosphorus Triamide with 1-Phenyl-3-methyl-4-ylidene-5-pyrazolones

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ORGANOPHOSPHORUS CHEMISTRY 34[1]. THE REACTION OF ALKYL PHOSPHITES AND HEXAMETHYLPHOSPHORUS TRIAMIDE WITH 1-PHENYL-3-METHYL-4-YLIDENE-5-PYRAZOLONES

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*1-Phenyl-3-methyl-4-ylidene-5-pyrazolones (**1a–c**) produce the respective 1:1 phosphonate adducts (**4a–i**) upon reaction with the appropriate dialkyl phosphites (**2a–c**). The reaction of **1a–c** with trialkyl phosphites (**3a–c**) proceeds only in presence of water, also to give phosphonates **4a–c** almost exclusively. Hexamethylphosphorus triamide (**3d**) was successfully utilized to introduce the bis(dimethylamino)-phosphoryl function in the α,β-unsaturated carbonyl moiety in **1a–c**, producing phosphoramidates **15a–c**. Possible reaction mechanisms were discussed. Compatible elemental and spectroscopic results were recorded for the new products.*

Keywords: Alkyl phosphites; hexamethylphosphorus triamide; phosphonates; phosphoromidates; reaction mechanism; ylidene pyrazolones

INTRODUCTION

In the line with our search for new organophosphorus compounds derived from heterocycles[2,3] for evaluating their pesticidal activity, we have now studied the reaction of 1-phenyl-3-methyl-4-ylidene-5-pyrazolones (**1a–c**) with dialkyl phosphites (**2a–c**), trialkyl phosphites (**3a–c**) and with hexamethylphosphorus triamide (**3d**) (see Figure 1). Ylidenes **1a** and **1c** are now prepared for the first time. It is also worthy to mention that certain phosphorylated pyrazole derivatives are known to evoke antiinflammatory/antiarthritic activity.[4,5,6]

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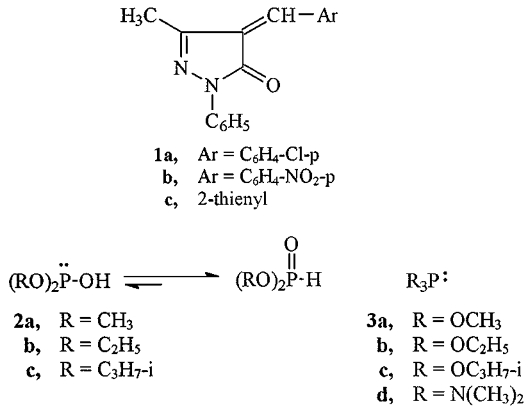

1a, Ar = C_6H_4-Cl-p
b, Ar = C_6H_4-NO_2-p
c, 2-thienyl

2a, R = CH_3
b, R = C_2H_5
c, R = C_3H_7-i

3a, R = OCH_3
b, R = OC_2H_5
c, R = OC_3H_7-i
d, R = $N(CH_3)_2$

FIGURE 1

RESULTS AND DISCUSSION

In an earlier investigation,[7,8] it has been claimed that 1-phenyl-3-methyl-4-benzylidene-5-pyrazolone (**1**, Ar=C_6H_5) reacts with dimethyl phosphite (**2a**) in the absence of solvent at 120°C yielding only a glassy solid which could not be recrystallized. On the other hand, it has been now found that 1-phenyl-3-methyl-4-(*p*-chlorobenzylidene)-5-pyrazolone (**1a**) reacts with dimethyl phosphite (**2a**) in the absence of solvent at 100°C to give a crystalline 1:1 adduct formulated as 1-phenyl-3-methyl-4-[(α-p-chloro-phenyl-α-dimethoxyphosphoryl)methyl]-5-hydroxypyrazole (**4a**) on the following basis:

(a) Elementary analyses and molecular weight determination (MS) corresponded to $C_{19}H_{20}ClN_2O_4P$;
(b) Positive chemical shift at δ 31.55 was recorded [^{31}P-NMR spectrum (vs 85%) H_3PO_4)] confirming the presence of a *phosphorus-to-carbon* linkage (phosphonate group).[9,10] (c) The strong carbonyl band present in the IR spectrum of **1a** at 1680 cm^{-1} was absent in the spectrum of **4a**. However, the spectrum showed strong bands at 1630 (C=N), 1580, 1520 (C=C), 1240 (P=O), 1000 (P—O—CH_3)[10,11] and at 760 cm^{-1} (Cl—Ar). (d) Compound **4a** is also readily soluble in 10% NaOH solution.

On this basis, an alternative pyrazolone structure like **5** (R = CH_3) (see Figure 2) can be excluded. (d) The ^{1}H-NMR spectrum of **4a** ($CDCl_3$, δ ppm) showed protons of the OCH_3 groups attached to phosphorus as two doublets (each with $^3J_{HP}$ = 12 Hz) at 3.70 and 3.40. Apparently,

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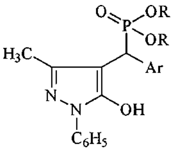

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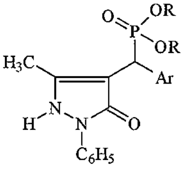
4a Ar = p-ClC$_6$H$_4$ R = CH$_3$
b Ar = p-ClC$_6$H$_4$ R = C$_2$H$_5$
c Ar = p-ClC$_6$H$_4$ R = i-C$_3$H$_7$
d Ar = p-NO$_2$C$_6$H$_4$ R = CH$_3$
e Ar = p-NO$_2$C$_6$H$_4$ R = C$_2$H$_5$
f Ar = p-NO$_2$C$_6$H$_4$ R = i-C$_3$H$_7$
g Ar = 2-thienyl R = CH$_3$
h Ar = 2-thienyl R = C$_2$H$_5$
i Ar = 2-thienyl R = i-C$_3$H$_7$



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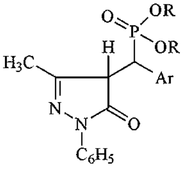

6

Ar and R as in **4**

FIGURE 2

the asymmetry of the molecule due to the presence of a stereo-centre would render the two methoxyl groups diastereotropic and hence anisochronous; resulting thus in the observed splitting pattern.[12] The spectrum also showed the P—CH proton as a doublet ($^2J_{HP} = 25$ Hz) at 4.20 ppm. Protons of the CH$_3$ group of the pyrazole ring appeared as a singlet at 2.10. A multiplet due to the phenyl- and OH-protons (10 H) appeared in the region 7.90–7.15 wherein emerge two doublets (each with $J_{HH} = 9$ Hz) due to protons of the p-chlorophenyl moiety (4H) at 7.75 and 7.40. On this basis, an alternative structure like **6** (R = CH$_3$) is excluded since the ^{1}H-NMR spectrum reveals the absence of the doublet-signals expected for the methine proton on the pyrazolone ring. (e) The mass spectrum of **4a** showed a molecular ion peak at m/z 406 (2.12%). Loss of the P(O)(OCH$_3$)$_2$ radical from M$^+$ yielded cation a at m/z 297 (33.57%), while loss of a neutral HP(O)(OCH$_3$)$_2$ molecule from M$^+$ afforded the radical cation b at m/z 296 (100%) (see Figure 3). The latter ion is also found as the molecular ion peak in the mass spectrum of **1a** itself. This

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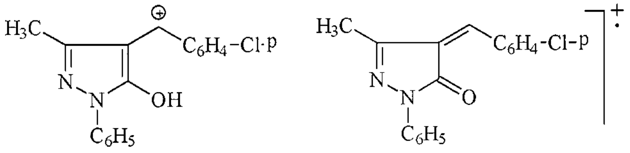


a
m/z 297 (299)

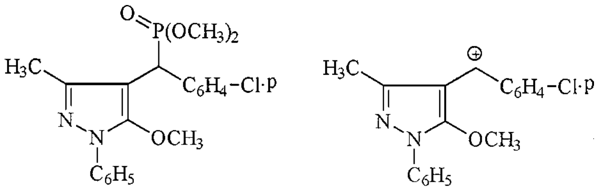
b
m/z 296 (298)

FIGURE 3

behaviour of **4a** under electron impact parallels its thermolysis under reduced pressure which affords **1a** and dimethyl phosphite (**2a**); (see Experimental Section.)

Addition of **4a** to a suspension of metallic sodium in benzene followed by treatment of the mixture with methyl iodide at the reflux temperature, afforded 1-phenyl-3-methyl-4-[(α-p-chlorophenyl-α-dimethoxyphosphoryl)methyl]-5-methoxypyrazole (**7**). Correct elemental analyses and molecular weight determination (MS) for **7** corresponded to $C_{20}H_{22}ClN_2O_4P$. Its IR spectrum (KBr) showed bands at 1350 (P=O, free)[10] and at 1050 (P—O—CH_3).[10] The ^{1}H-NMR of **7** ($CDCl_3$, δ ppm) showed protons of the OCH_3 groups attached to phosphorus as two doublets (each with $^3J_{HP} = 12$ Hz) at 3.05 and 3.20. The spectrum showed the P—<u>CH</u> proton as a doublet ($^2J_{HP} = 24$ Hz) at 4.10 ppm. The CH_3 group on the pyrazole ring appeared as a singlet at 2.05 ppm. A singlet due to the OCH_3 protons appeared at 3.10 ppm and a multiplet due to the aromatic groups (9H) appeared in the region 7.40–6.80 ppm. The mass spectrum of **7** showed the molecular ion peak at m/z 420 (422). Loss of the $^{\cdot}P(O)(OCH_3)_2$ radical from M^+ afforded the base peak (cation *c*) at m/z 311 (313) (see Figure 4).

The phosphonate 1:1 adducts **4b–i** could also be obtained upon heating compounds **1a–c** with the appropriate dialkylphosphite (**2a–c**) at 100°C in the absence of solvent. They dissolve freely in 10% aqueous sodium hydroxide solution and regernerate the corresponding starting



7

c
m/z 311 (313)

FIGURE 4

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materials (**1** + **2**) upon thermolysis under reduced pressure. Consistent elementary and spectroscopic measurements were recorded for **4b–i**.

Reactions of **1a–c** with trialkyl phosphites (**3a–c**) in the absence of solvent at 100°C were rather sluggish and the reactants were recovered practically unchanged. On the other hand, they proceeded smoothly when a protonating agent (H_2O) was introduced in the medium, yielding crystalline products. The latter proved to be identical (m.p., mixed m.p., and comparative IR and ^{1}H-NMR spectra) with **4a–i** respectively; previously prepared by reacting **1a–c** with the appropriate dialkyl phosphite (**2a–c**) vide infra.

A mechanism for the formation of compounds **4a–i** via reacting **1a–c** with trialkyl phosphites (**3a–c**) is depicted in Scheme 1. This involves primary nucleophilic attack by the phosphite-phosphorus on the ylidene-carbon atom of **1** to give the $\underline{C}$-phosphonium betain **8** (path A). The dipolar structure **8** can add elements of water in the medium as do many phosphobetain structures[13–15] to give intermediate **9** (pentacovalent phosphorus). The latter decomposes via expulsion of ROH to give compounds **4a–i**. Initial formation of a $\underline{C}$-phosphonium betain such as **10** in these reactions (path B) may be ruled out. Addition of elements of water to intermediate **10** would give the transient **11**. Solvolysis of the latter would produce phosphorylated pyrazolone structures (**12**) instead of the observed phosphorylated pyrazoles **4**.

In the same sense, the reaction of hexamethylphosphorustriamide (**3d**) with ylidenes **1a–c** proceeded only in the presence of water to give phosphonate adducts for which structures **15a–c** were respectively assigned. Apparently, the $\underline{C}$-phosphonium betain **13** initially formed adds elements of H_2O to afford intermediate **14**. Decomposition of the latter via expulsion of $(CH_3)_2NH$ would afford the final products (**15a–c**) (Scheme 2).

Analytical and spectroscopic measurements for **15a–c** are compatible with the assigned structures.

The mass spectrum of **15a** showed the base peak at m/z 297 (ion *a*); due to loss of the $O{=}P[N(CH_3)_2]$ radical from the molecular ion peak. Loss of the same radical from the parent peak (m/z 404, 75.60%) in the mass spectrum of **15c** also afforded the base peak (m/z 269, ion $\underline{d}$). On the other hand, the base peak in the mass spectrum of **15b** appeared at m/z 307 (ion $\underline{e}$) due to loss of a neutral $H(O)P[N(CH_3)_2]$ molecule from the parent ion peak (m/z 443, 6.84%). In all spectra, a prominent peak was shown at m/z 135 due to the dimethylaminophosphoryl cation (ion $\underline{f}$).

The insecticidal activities of some selected new phosphonates were tested against *Spadoptera littoralis*, *Aphis craccivora*, and *Tetranychus urtecae*. The results will be published elsewhere later.

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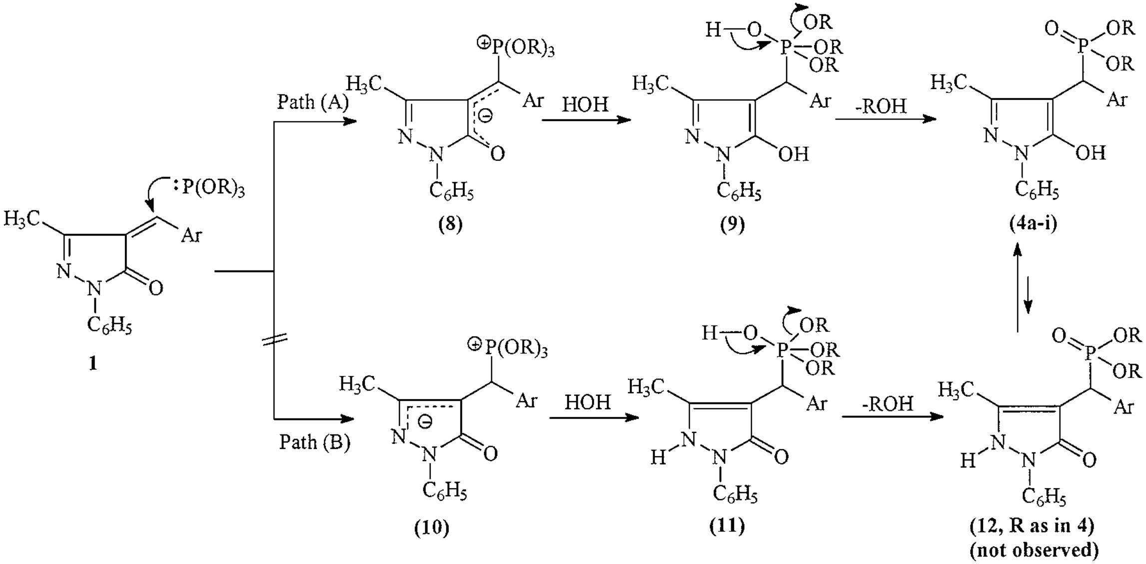

SCHEME 1

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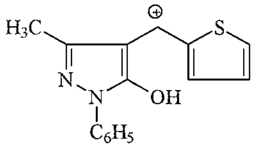
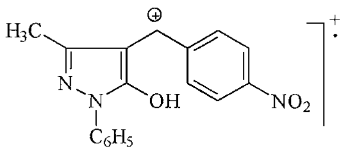


d



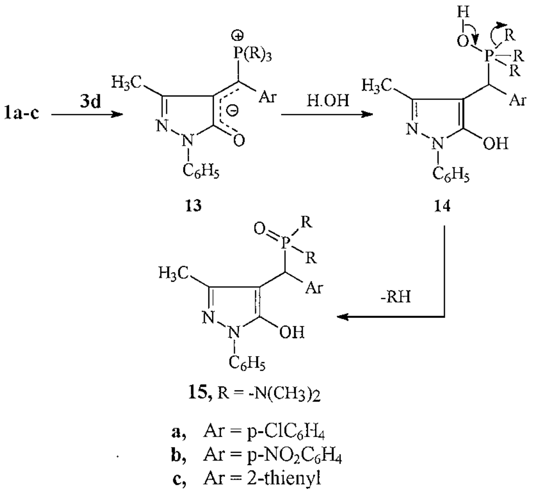
e

$\oplus\overset{\overset{\displaystyle O}{\|}}{P}[N(CH_3)_2]$

f

CONCLUSION

Results of the present work show that dialkyl phosphites (**2**) attack the 4-ylidene-5-pyrazolone derivatives (**1**) essentially at the —CH=C—C=O system and not at the —CH=C—C—=N— system, to give the respective pyrazolyl dialkyl phosphonates (**4**). The latter compounds contribute to members of the group of phosphorylated heterocycles which belong to a variety of active principles frequently used as pesticides.[16–18] Though the reaction of **1** with trialkyl phosphites is rather sluggish, it can be directed to produce phosphonates **4** by admitting a protonating agent like water, in the reaction medium. Besides, the present study describes a successful approach for utilizing hexamethylphosphorus triamide (**3d**) to introduce a bis [dimethylamino]-phosphoryl function (cf. **15a–c**) in α,β-unsaturated carbonyl systems. To the best of our knowledge, this finding explores a new era in the chemistry of phosphoramidate compounds.



SCHEME 2

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded in KBr by using a JASCO FT/IR-3000 E Infracord or Bomen-Michelson Infracord. The ^{1}H-NMR spectra were measured on a Jeol EX-270 Spectrometer using TMS as an internal standard. The ^{31}P-NMR spectra were recorded (vs 85% H_3PO_4) with a Bruker Spectrometer. The mass spectra were determined at 70 eV on a Finnigan-MAT SSQ 7000 Spectrometer. The phosphorus reagents **2a–c** and **3a–d** were available from Aldrich Co., and were freshly distilled before use. Compound **1b**[19] was prepared according to an established procedure.

Preparation of 1-phenyl-3-methyl-4-(p-chlorobenzylidene)-5-pyrazolone (1a)

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To 1-phenyl-3-methyl-5-pyrazolone (0.04 mol) dissolved in glacial acetic acid (10 ml), was added p-chlorobenzaldehyde (0.05 mol) in 10 ml glacial acetic acid. The mixture was kept at room temperature for 24 h then diluted with water till turbidity appeared. After cooling, the precipitated material was filtered off, washed with water, dried, and recrystallized from ethanol to give **1a** as red crystals, m.p. 160–162°C (dec.), yield: 70%. Anal. Calcd. for $C_{17}H_{13}ClN_2O$: C, 68.80; H, 4.41; Cl, 11.94; N, 9.44. Found: C, 68.55; H, 4.71, Cl, 12.14; N, 9.63%. IR (KBr, cm^{-1}): Bands at 1680 (C=O), 1620, 1590, 1520 (C=C) and 718 (Cl—Ar). ^{1}H-NMR ($CDCl_3$, δ ppm): 2.35 (3H, CH_3, s) and 8.5–7.05 (10H, aromatics + olefinic proton, m). MS (m/z, %): Ion peaks at 296 (298) (M^+, 100%) and 185 (M—$\cdot C_6H_4$—Cl—p, 60%).

Similarly, 1-phenyl-3-methyl-4-thienylidene-5-pyrazolone (**1c**) was obtained from ethanol as brown crystals, m.p. 95–97 (dec.), upon heating 1-phenyl-3-methyl-5-pyrazolone (0.04 mol) and 2-thiophene aldehyde (0.05 mole) in glacial acetic acid (10 ml) at 140°C for 14 h. Anal. Calcd. for $C_{15}H_{12}N_2OS$: C, 67.14; H, 4.50; N, 10.44; S, 11.94. Found: C, 67.45; H, 4.31; N, 10.13; S, 11.77%. IR (KBr, cm^{-1}): Bands at 3067 (CH, aromatic), 1681 (C=O) and 1616 (C=C). MS (m/z, %): Ion peaks at 268 (M^+, 100%) and 185 (M—C_4H_3S, 8.96%).

Reaction of 1-Phenyl-3-methyl-4-ylidene-5-pyrazolones (1a–c) with Dialkyl Phosphites (2a–c)

General Procedure

A mixture of **1a,b**, or **c** (0.01 mol) and dialkyl phosphite (dimethyl-, diethyl-, or diisopropyl phosphite, 5 ml) was heated in the absence of solvent at 100°C for 4–8 h. After removing the volatile materials in vacuo, the residue was triturated with light petroleum and left to cool. The solid formed was collected and recrystallized from a suitable solvent to give compounds **4a–i**. Physical, analytical and spectral data for compounds **4a–i** are presented in Tables I and II.

Action of Heat on Phosphonate 4a

Compound **4a** (0.30 g), was heated in a cold finger sublimator at 150°C (bath temperature) under reduced pressure (5 mm/Hg) for 15 min. The compound that sublimed was collected (85%), recrystallized from ethanol to give red crystals, proved to be 1-phenyl-3-methyl-4-(p-chloro-benzylidene)-5-pyrazolone (**1a**) (mp., mixed m.p. 160–162, and comparative IR spectra).

Dimethyl phosphite (**2a**) was detected in the receiver by the development of a violet color on addition of 3,5-dinitrobenzoic acid in the presence of alkali.[20]

The Reaction of Phosphonate 4a *with Methyl Iodide*

A mixture of **4a** (0.2 g) and Na metal (0.2 g) suspended in benzene (50 ml) was left at room temperature under good stirring for 8 h, treated with methyl iodide (5 g) then refluxed for 10 h. The inorganic material was filtered and washed with a small amount of dry acetone. After evaporation of the filtrate and washings to dryness, the residue was recrystallized from cyclohexane to give **7** as colorless crystals, m.p. 80°C, yield: 80%.

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Reaction of 1-Phenyl-3-methyl-4-ylidene-5-pyrazolones (1a–c) with Trialkyl Phosphites (3a–c)

General Procedure

A mixture of **1a,b**, or **c** (0.005 mole) and trialkyl phosphite (trimethyl-, triethyl-, or triisopropyl phosphite, 3 ml) was heated at 100°C for 4–6 h in the absence of solvent and in the presence of H_2O (1 ml). After evaporation of the volatile materials in vacuo, the residual substance was treated with light petroleum (15 ml). The solid material was collected and recrystallized from the appropriate solvent to give **4a–i**. Yields of **4a–i** prepared by this method ranged between 70–80%.

Reaction of Hexamethylphosphorus Triamide (3d) with 1-Phenyl-3-methyl-4-ylidene-5-pyrazolones (1a–c)

General Procedure

A mixture of **3d** (0.01 mol) and the ylidene-pyrazolone derivative **1a** (**1b** or **1c**) (0.01 mol) was heated in absence of solvent at 100°C for

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TABLE I Physical, Analytical, and IR Spectral Data of Compounds **4a–i**, **7**, and **15a–c**

				Anal. (Calcd./Found)						M^+	IR cm^{-1b}		
Comp.	Yield^a (%)	m.p. (°C)	Mol. form. (m. wt.)	C	H	Cl	N	P	S	m/z (%)	C=N	P=O	P—O—C
4a	75	100–102	$C_{19}H_{20}ClN_2O_4P$	56.09	4.94	8.71	6.88	7.61		406	1580	1240	1110
			(406.80)	55.84	4.56	9.01	6.55	7.21		<5			
4b	70	120–121	$C_{21}H_{24}ClN_2O_4P$	58.00	5.56	8.15	6.44	7.12		434	1620	1340	1050
			(434.86)	58.41	5.87	8.21	6.87	7.49		(<5)			
4c	80	110–113	$C_{23}H_{28}ClN_2O_4P$	59.67	6.09	7.65	6.05	6.69		462	1610	1340	1000
			(462.91)	60.04	5.99	7.85	6.14	6.88		(19.63)			
4d	80	140–142	$C_{19}H_{20}N_3O_6P$	54.67	4.83		10.06	7.42		417	1620	1345	1040
			(417.35)	55.01	4.58		10.34	7.54		(66.12)			
4e	80	100–103	$C_{21}H_{24}N_3O_6P$	56.62	5.43		9.43	6.95		445	1630	1345	1020
			(445.41)	56.43	5.88		9.00	7.02		(38.47)			
4f	85	170–171	$C_{23}H_{28}N_3O_6P$	58.34	5.96		8.87	6.54		473	1620	1345	1010
			(473.46)	58.75	6.26		8.52	6.90		(33.05)			
4g	75	60–62	$C_{17}H_{19}N_2O_4PS$	53.96	5.06		7.40	8.18	8.47	378	1620	1340	1030
			(378.38)	53.56	5.46		7.82	8.50	8.86	(59.47)			
4h	80	70–72	$C_{19}H_{23}N_2O_4PS$	56.14	5.70		6.89	7.62	7.88	406	1610	1340	1010
			(406.44)	56.51	5.45		7.01	7.42	7.55	(<5)			
4I	85	75–77	$C_{21}H_{27}N_2O_4PS$	58.05	6.26		6.44	7.12	7.37	434	1620	1340	1000
			(434.49)	58.38	6.58		6.88	7.50	7.80	(<5)			
7	70	100–102	$C_{20}H_{22}ClN_2O_4P$	57.08	5.26	8.42	6.65	7.36	—	420	1620	1350	1050
			(420.83)	57.43	5.57	8.80	6.90	7.73		(<5)			
15a	75	80–82	$C_{21}H_{26}ClN_4O_2P$	58.26	6.05	8.18	12.94	7.15	—	432	1600	1360	—
			(432.89)	58.46	5.91	8.36	13.01	7.44		(52.50)			
15b	80	70–72	$C_{21}H_{26}N_5O_4P$	56.88	5.91		15.79	6.98	—	443	1600	1320	—
			(443.44)	57.07	5.73		15.43	7.02		(6.84)			
15c	80	100–102	$C_{19}H_{25}N_4O_2PS$	56.42	6.23		13.85	7.65	7.92	404	1590	1360	—
			(404.47)	56.11	6.52		13.51	7.34	8.01	(75.60)			

[a] Approximated.

[b] The OH-group absorbed around 3400 cm^{-1} in the IR-spectra of **4b–i** and **15a–c**.

[c] Solvents of recrystallization **4b**,**c**, **7**, **15c** (cyclohexane), **4a**,**e**,**f** (pet. Ether 40–60°C), **4d**,**g** (pet. Ether 60–80°C), **4h**,**i**, **15a**,**b** (ethyl acetate-ether).

[d] The IR-spectra of **15a–c** showed the —N(CH$_3$)$_2$ group absorption around 2850 cm^{-1}.[9,10]

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TABLE II ^{31}P- and ^{1}H-NMR Spectral Data of Compounds **4b–i** and **15a–c**

Comp.	^{31}P-NMR	^{1}H-NMR[a]
4b	29.85	1.2 [d of t, 6H, $\mathrm{P{-}(O{-}C{-}\underline{CH_3})_2}$], 2.15 (s, 3H, $\mathrm{\underline{CH_3}}$), 3.95 (d of quint., 4H, $\mathrm{P{-}(O{-}\underline{CH_2}{-}C)_2}$, 4.25 (d, 1H, $^2J_{HP} = 27$ Hz, $\mathrm{p{-}\underline{CH}}$), 7.15–8.05 (m, 10H, 9H, aromatics, and $\mathrm{\underline{OH}}$).
4c	28.00	1.3 [m, 12H, $\mathrm{P{-}(O{-}C{-}\underline{CH_3})_2)_2}$], 2.15 (s, 3H, $\mathrm{\underline{CH_3}}$), 4.10 (d, 1H, $^2J_{HP} = 24$ Hz, $\mathrm{p{-}\underline{CH}}$), 4.50 (d of sept., 2H, $\mathrm{P{-}(O{-}\underline{CH}{-}C)_2}$, 7.15–8.05 (m, 9H, aromatics), 10.40 (s, $\mathrm{\underline{OH}}$).
4d	31.20	2.05 (s, 3H, $\mathrm{\underline{CH_3}}$), 3.55, 3.85 (2d, $^3J_{HP} = 12$ Hz, 6H, $\mathrm{P{-}(O{-}\underline{CH_3})_2}$, 4.90 (d, 1H, $^2J_{HP} = 27$ Hz, $\mathrm{P{-}\underline{CH}}$), 7.20–8.30 (m, 9H, aromatics), 11.80 (bs, $\mathrm{\underline{OH}}$).
4e		1.20 [d of t, 6H, $\mathrm{P{-}(O{-}C{-}\underline{CH_3})_2}$], 2.25 (s, 3H, $\mathrm{\underline{CH_3}}$), 4.0 (d of quint., 4H, $\mathrm{P{-}(O{-}\underline{CH_2}{-}C)_2}$, 4.35 (d, 1H, $^2J_{HP} = 27$ Hz, $\mathrm{P{-}\underline{CH}}$), 7.20–8.30 (m, 10H, 9H, aromatics, and $\mathrm{\underline{OH}}$).
4f	8.61	1.20 [m, 12H, $\mathrm{P{-}(O{-}C{-}\underline{CH_3})_2)_2}$], 2.15 (s, 3H, $\mathrm{\underline{CH_3}}$), 4.30 (d, 1H, $^2J_{HP} = 27$ Hz, $\mathrm{P{-}\underline{CH}}$), 4.65 (d of sept., 2H, $\mathrm{P{-}(O{-}\underline{CH}{-}C)_2}$, 7.20–8.25 (m, 9H, aromatics), 11.50 (s, $\mathrm{\underline{OH}}$).
4g		2.20 (s, 3H, $\mathrm{\underline{CH_3}}$), 3.60, 3.75 (2d, $^3J_{HP} = 9$ Hz, 6H, $\mathrm{P{-}(O{-}\underline{CH_3})_2}$, 4.50 (d, 1H, $^2J_{HP} = 27$ Hz, $\mathrm{P{-}\underline{CH}}$), 6.90–7.85 (m, 8H, aromatics, and thiophene), 11.00 (bs, $\mathrm{\underline{OH}}$).
4h	26.30	1.20 [d of t, 6H, $\mathrm{P{-}(O{-}C{-}\underline{CH_3})_2}$], 2.20 (s, 3H, $\mathrm{\underline{CH_3}}$), 4.00 (d of quint., 4H, $\mathrm{P{-}(O{-}\underline{CH_2}{-}C)_2}$, 4.50 (d, 1H, $^2J_{HP} = 24$ Hz, $\mathrm{P{-}\underline{CH}}$), 6.90–8.00 (m, 8H, aromatics, and thiophene), 10.40 (s, $\mathrm{\underline{OH}}$).
4i		1.30 [m, 12H, $\mathrm{P{-}(O{-}C{-}\underline{CH_3})_2)_2}$], 2.40 (s, 3H, $\mathrm{\underline{CH_3}}$), 4.10 (d of sept., 2H, $\mathrm{P{-}(O{-}\underline{CH}{-}C)_2}$, 4.50 (d, 1H, $^2J_{HP} = 24$ Hz, $\mathrm{P{-}\underline{CH}}$), 6.90–7.70 (m, 9H, aromatics, thiophene, and $\mathrm{\underline{OH}}$).
15a	12.00	2.10 (s, 3H, $\mathrm{N{=}C{-}\underline{CH_3}}$), 2.30, 2.60 [2d, each with $^3J_{HP} = 9$ Hz, 12 H, $\mathrm{{-}[N(CH_3)_2]_2}$], 4.15 (d, 1H, $^2J_{HP} = 18$ Hz, $\mathrm{P{-}\underline{CH}}$), 7.10–7.90 (m, 9H, aromatics), 13.25 (s, 1H, $\mathrm{\underline{OH}}$).
15b		2.10 (s, 3H, $\mathrm{N{=}C{-}\underline{CH_3}}$), 2.30, 2.65 [2d, each with $^3J_{HP} = 9$ Hz, 12 H, $\mathrm{{-}[N(CH_3)_2]_2}$], 4.30 (d, 1H, $^2J_{HP} = 18$ Hz, $\mathrm{P{-}\underline{CH}}$), 7.10–8.25 (m, 9H, aromatics), 10.15 (s, 1H, $\mathrm{\underline{OH}}$).
15c		2.15 (s, 3H, $\mathrm{N{=}C{-}\underline{CH_3}}$), 2.45, 2.70 [2d, each with $^3J_{HP} = 9$ Hz, 12 H, $\mathrm{{-}[N(CH_3)_2]_2}$], 4.50 (d, 1H, $^2J_{HP} = 18$ Hz, $\mathrm{P{-}\underline{CH}}$), 6.90–7.85 (m, 8H, aromatics, and thiophene), 12.90 (s, 1H, $\mathrm{\underline{OH}}$).

[a] Run in $CDCl_3$. The OH-signals are D_2O exchangeable.

2 h. Water (1 ml) was then added and the mixture is further heated for 2 h. After evaporation of the volatile materials in vacuo, the solid material was collected and recrystallized from the appropriate solvent to give **15a–c**. For physical, analytical and spectroscopic data of **15a–c**, cf. Table I and II.

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