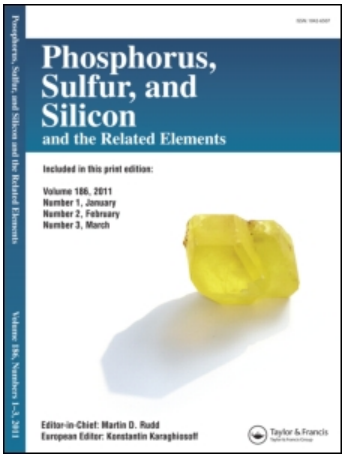

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PHOSPHORYLATION OF α-OXIMINOACETONITRILE

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PHOSPHORYLATION OF α-OXIMINOACETONITRILE

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The synthesis of some phosphonylated and phosporylated oximes is described. The structure of the compounds has been established by means of spectroscopic methods and elemental analysis.

Keywords: phosphonylated and phosphorylated oximes; oximes; dichlorophosphite; dichlorophosphate; dichlorothiophosphite; dichlorothiophosphate; IR; MS; NMR assignments

INTRODUCTION

The chemistry and structural exploration of oximes (oximinic compounds) is an issue of great present interest because of their biological activity (e.g. reactivators of acetylchlolinesterase inhibited by organophosphorus poisoning[1-2]). These compounds, belonging to the group of carbamoyl oximes, have been described as insecticides and nematocides[3]. Oximinoesters of phosphoric and thiophosphoric acids are important agrochemicals[4]. The study of inter- and intramolecular interactions of these compounds was recently reviewed[5].

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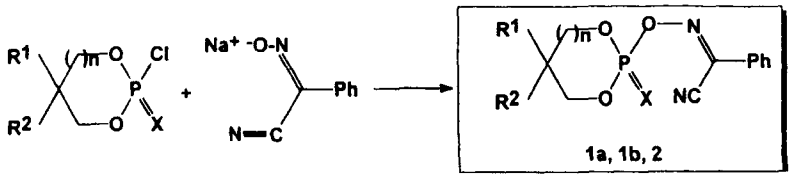
RESULTS AND DISCUSSION

The presence of *two* oximinic moyeties in the same molecular environment is expected to radically change the physico-chemical features and hence biological potential of the compounds. Obviously, these changes should be dependent upon geometrical factors and structures of the phosphorus substituents.

1. Synthesis

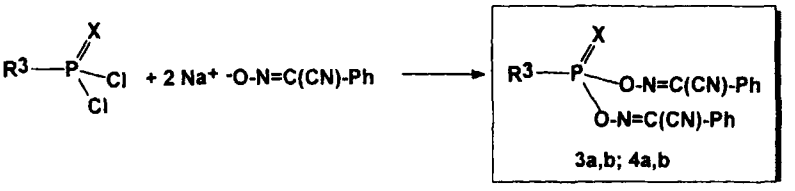
In order to evaluate the above premisy, seven novel oximines were prepared (**Schemes 1, 2**); in this paper, it is our intention to report their synthesis as well as essential spectroscopic data.



	R^1	R^2	n	X	Time(hr)	Yield (%)
1a	Me	Me	1	O	0.5	41
1b	Me	Me	1	S	2.0	40
2	Me	H	0	S	2,0	62

SCHEME 1

All compounds **1–4** have been isolated as colorless crystalline solids in satisfactory yields (40–60%). The synthesis were performed in dry media with mild conditions (see **EXPERIMENTAL**). We note here the expected lower reactivity of thioderivatives (longer reaction times), compared with the oxygenated ones, regarding the ability of the **X=O** group to activate the nucleophilic displacement of chlorine.



	R^3	X	Time (hr)	Yield (%)
3a	*c*-C_6H_{11}	O	2.0	40
3b	*c*-C_6H_{11}	S	3.0	42
4a	EtO	O	2.0	45
4b	EtO	S	3.0	45

SCHEME 2

2. Structural assignments

IR-spectra

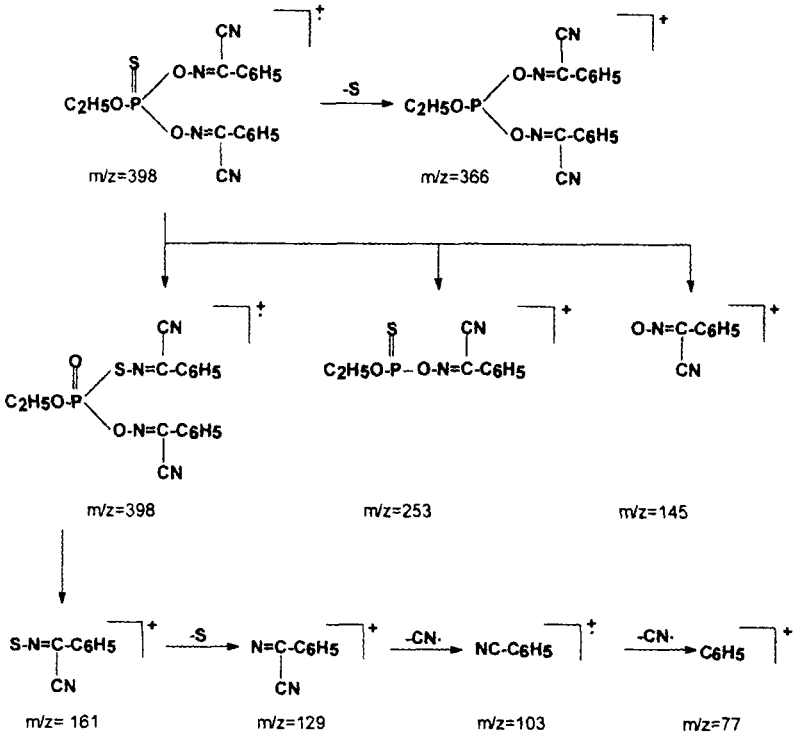
The peak at about 2240cm^{-1}, assigned to ν_{CN}[6,7] has been clearly detected in all IR-spectra. The strong bands located in the 910 – 930cm^{-1} region have revealed the presence of the new oxime **N-O** bond[8,9]. This assumption is supported by the location at 980cm^{-1} and 1000cm^{-1} of this absorbtion for free α-cyanoximes and their sodium salts respectively. These lower values showed the strong interaction between the oxime group and the phosphoryl (or thiophosphoryl) group.

The $\nu_{P=O}$ band at about 1300cm^{-1} has been considered as characteristic. Therefore, in the analogous **P=S** compounds, the $\nu_{P=S}$ band has been identified around 830cm^{-1} and 640cm^{-1} by comparison only (inspection of spectra has showed both these bands as absent in the case of **P=O** compounds)[10–13].

Mass spectra

Mass spectra have exhibited in all cases the molecular peak M^+. The already reported fragmentation of the cyanoxi group[14] has been recog-

nized for all series **1–4.** The base peak has been the benzene group, except compound **3a.** The fragmentatiom of compounds **1a, b** has occurred with elimination of the high intensity $C_5H_9^+$(m/z = 69) ion. Due to the successive loss of a methylene group from this fragment, formation of $C_4H_7^+$ (m/z = 55) and $C_3H_5^+$ (m/z = 41) has been observed. The loss of formaldehyde from all cyclic compounds **1, 2** is also characterisric[15] as well as the desulfurisation under electronic impact of the molecular ions of the **P**-sulphides. Finally, the degradation pathways of the compounds **3–4** have confirmed the postulated structures (the presence in the molecules of ethoxy, cyclohexyl, and cyanoxy groups). The fragmentation pattern of the compound **4b** is given as a typical example **(Fig.1, Scheme 3)**



SCHEME 3

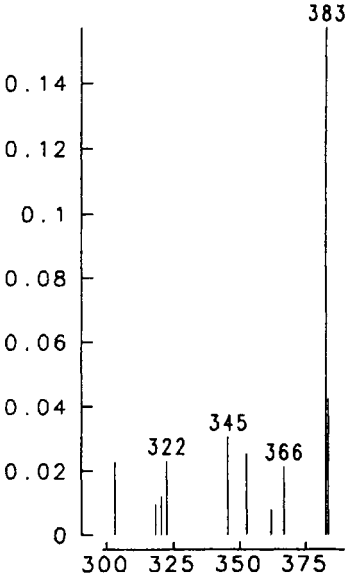


FIGURE 1 Mass spectrum of the compound **4b**(detail)

NMR spectra[16]

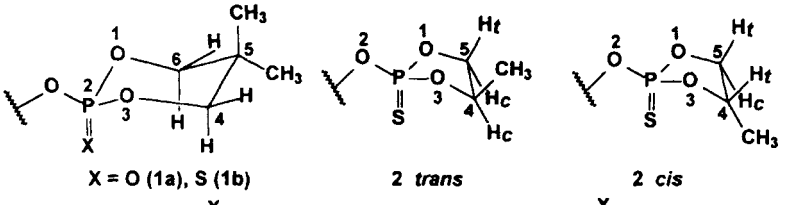
The structure of the oximines **1–4** has been fully confirmed by ^{1}H, ^{31}C and ^{31}P-NMR spectroscopy. Some peculiar data will be discussed in this section. The presence of phosphorus as the basic heteroatom is confirmed by the NMR – data listed in **Table I.**

The following structural assignments have been considered worthy to be discussed:

The 2-substituted-5,5-dimethyl-1,3,2-dioxaphosphorinanes **1a, 1b** are chair shaped anomeric structures because distinct AMX systems have been observed in the ^{1}H-NMR spectrum concerning the **C-4(6)** diastereotopic methylene (the diastereotopicity $\Delta\delta_{H4(6)a\text{-}H4(6)e}$ ranges between 0.23ppm (**1a**) and 0.30ppm (**1b**). Accordingly, distinct singlets have been found for the **C-5** axial and equatorial methyl groups (diastereotopicity $\Delta\delta_{Me(a)\text{-}Me(e)} = 0.42$ppm in both **1a** and **1b**). The diastereotopicity of the same methyl groups in the ^{13}C-NMR spectra is 1.7ppm (**1a**) and 1.3ppm (**1b**). As depicted in **Table I,** the $^{3}J_{P\text{-}H}$ couplings have indicated the expected relationship $^{3}J_{P\text{-}Ha} < {}^{3}J_{P\text{-}He}$ and their sum increases from 22.7 to

25.2Hz, by their change from 2-oxo (**1a**) to 2-thionoderivative (**1b**). These data are in agreement with the axial position of the =**X** 2-substituent.

TABLE I ^{31}P Chemical shifts (δ. ppm) and Coupling constants ($^{n}J_{H\text{-}P}$ and $^{n}J_{C\text{-}P}$, Hz) for the compounds *1–4* (solvent $CDCl_3$ except 4a-DMSO-d_6)



X = O (3a), S (3b) X = O (4a), S (4b)

	$^{n}J_{H\text{-}P}$			$^{n}J_{C\text{-}P}$			
No.	δ	^{2}J	^{3}J	^{1}J	^{2}J	^{3}J	^{4}J
1a	-10.10	-	22.7(H-4e-6e) 0.0(H-4a-6a)	-	7.2 (C-4–6)	6.8(C-5) 14.4 (>C=N-)	-
1b	58.57	-	22.7(H-4e-6e) 2.5(H-4a-6a)	-	9.0 (C-4–6)	6.5(C-5) 15.6 (>C=N-)	-
2-trans	81.65	-	2.0(H-4c) 4.4(H-5c) 21.4(H-5t)	-	-	6.3 and 7.1(-CH_3) 12.6 and 12.8 (>C=N-)	-
2-cis	81.30	-	10.1 (H-4t) 5.1(H-5c) 13.0(H-5t)	-	-		
3a	39.90	-	-	124.5	16.5	13.3 (>C=N-) 15.7 (C-3–5)	4.6(C-4)
3b	59.33	-	-	94.2	18.3	14.0 (>C=N-)	19.4(C-4)
4a	0.09	7.0	7.2	-	5.3	6.8 (-CH_3)	-
4b	68.31	11.5	-	-	6.0	6.1 (-CH_3) 16.6 (>C=N)	-

The 1,3,2-dioxaphospholane **2** has been isolated as a racemic diastereomeric mixture (***2-cis*** and ***2-trans***) in a 1:2 molar ratio resp. as proved by the ^{31}P-NMR spectrum where two doublets of quartets have been identified. Discrimination between diastereomers is based on the well separated AMX systems (**H-4 H-*5c*H-*5t***; the **C-4** methyl group and the sulfur atom as reference and ring protons are labeled as *cis(c)* or *trans(t)* with respect to sulfur atom). Thus, in ***2-trans*** we have found $^{3}J_{cis\ \text{H-4c H-5c}}$ about 1Hz and $^{3}J_{trans}$ $H_{4c\ \text{H-}5t}$ = 8.7Hz, meanwhile, in the **2-*cis*** diastereomer the steric relationship gave $^{3}J_{cis\ \text{H4}t\ \text{H-}5t}$= 8.6Hz and $^{3}J_{trans\ \text{H-4}t\ \text{H-}5c}$ = 7.6Hz. These assignments are also supported by the $^{3}J_{\text{P-H}}$ values depicted in **Table I**.

Compounds **3a, b** are anomeric structures with the substituent in equatorial position, in agreement with the $^{n}J_{\text{P-C}}$ calculated values. The ^{31}P-NMR spectrum showed three slightly different cuplings (octet) $^{1}J_{\text{P-H-1a}}$, $^{2}J_{\text{P-H-2a}}$ and $^{2}J_{\text{P-H2e}}$ with the cyclohexyl protons, but their magnitude has been too small for pertinent assignment.

Finally, although our attempts to assign the configuration of the oximinic group *(syn* or *anti)*were unsuccessful, we believe that all syntheses have been totaly diastereoselective. Thus, both oximinic side chains have the same configuration because just one set of δ and J values have been found in each case. Compounds **4a, b** have exhibited the methylene α to $X=PO_3$ as enantiotopic, hence identical configurations of both oximinic ligands.

EXPERIMENTAL

Melting points are not corrected; they were measured with a heated silicon-oil bath.All synthesis were monitored by TLC (eluent dioxane : water = 9:1 v/v); each compound exhibited one single spot.

IR spectra were performed on KBr pellets on SPECORD IR 75 K. Zeiss Jena instrument.

Mass spectra were measured with a VARIAN MAT 711 (70eV) Instrument at Ruhr University, Department of Theoretical Organic Chemistry, Bochum, Germany.

All NMR spectra were performed with a Brucker AM 400 spectrometer, operating at 400MHz for ^{1}H and 100MHz for ^{13}C. ^{1}H chemical shifts were

measured to TMS as internal standard. ^{13}C chemical shifts are reported against the solvent peak. ^{31}P chemical shifts refer to the 85% H_3PO_4 as external standard. *The same coupling patterns* $^{n}J_{P\text{-}H}$ *were used as evidence in both* ^{31}P*- and* ^{1}H*-NMR spectra, in order to simplify discussion,* $^{n}J_{P\text{-}C}$ *values were measured in* ^{13}C*-NMR spectra only.*

2-(α-Oximinophenylacetonitril)-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane (1a).

2-Chloro-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane (9.2g 0.05mol), dissolved in dry diethyl (50mL) ether was treated, with stirring, at 20–25°C, with α-oximinophenylacetonitril sodium salt 8.4g(0.05mol). After 30min., the solvent was removed and water (200mL) was added to the residue to give a suspension. After filtering, the crude product was dissolved in benzene (100mL), dried over $MgSO_4$, and evaporated to dryness. Crystallization from diethyl ether yielded the pure product (6.0g, 41% yield); *m.p.* = 94–6°C. *Anal. calcd for* $C_{13}H_{15}N_2O_4P$: C 53.06%; H 5.13%; N 9.51%; P 10.52%; found: C 53.24%; H 5.13%; N 9.53%; P 10.69%. *IR spectrum* (cm^{-1}): 2220 (ν_{CN}), 1310 ($\nu_{P=O}$), 930 ($\nu_{N\text{-}O}$). *Mass spectrum* (m/z, %): 294, (25), $[M]^+$; 264, (11), $[M\text{-}CH_2O]^+$; 129, (55), $[C_6H_5(CN)C{=}N]^+$; 77, (100), $[C_6H_5]^+$; 69, (98), $[C_5H_9]^+$. *NMR Spectra* ($CDCl_3$) ; **^{31}P** (δ, ppm; ^{n}J, Hz): −10.10 (t, ^{3}J = 22.7Hz); **^{13}C**: 19.8 (s, -CH_3 ax.), 21.5 (s, -CH_3 eq.), 32.1 (d, C-5, ^{3}J= 6.8Hz), 79.1 (d, C-4, C-6, ^{2}J = 7.2Hz), 107.9 (s, -CN), 127.0 (s, *C-orto),* 127.2 (s, *C-meta),* 129.2 (s, *C-para),* 133.1 (s, *C-ipso),* 141.5 (d, >*C*=N-, ^{3}J= 14.5Hz); **^{1}H**: 0.86 (s, 3H, -CH_3 ax.), 1.28 (s, 3H, -CH_3 eq.), 4.00 (dd, 2H, H-4e, H-6e, ^{2}J= 10.6Hz, ^{3}J = 22.7Hz), 4.23 (d, 2H, H-4a, H-6a, ^{2}J = 10.6Hz), 7.00–8.00 (m, 5H, aromatic).

2-(α-Oximinophenylacetonitril)-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane (1b).

2-Chloro-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane (10.8g 0.05mol), dissolved in dry acetone (50mL) was treated with stirring, at 40°C, with α-oximinophenylacetonitril sodium salt 8.4g(0.05mol). After 2hr., the solvent was removed and water (200mL) was added to the residue to give a suspension. After filtering, the crude product was dissolved in benzene (100mL), dried over $MgSO_4$, and evaporated to dryness. Crystallization from diethyl ether yielded the pure product (6.7g, 40% yield);

m.p. = 115–6°C. *Anal. calcd. for* $C_{13}H_{15}N_2O_4PS$: C 50.31%; H 4.87%; N 9.02%; P 9.98%; found: C 50.23%; H 4.72%; N 9.26%; P 9.84%. *IR spectrum* (cm^{-1}): 2215 (ν_{CN}), 810, 640 ($\nu_{P=S}$), 905 (ν_{N-O}). *Mass spectrum* (m/z, %): 310, (17), $[M]^+$; 295, (0.2), $[M\text{-}CH_3]^+$; 129, (91), $[C_6H_5(CN)C{=}N]^+$; 77, (100), $[C_6H_5]^+$; 69, (62), $[C_5H_9]^+$. *NMR Spectra* ($CDCl_3$) ; **^{31}P** (δ, ppm; ^nJ,Hz): 58.57 (tt, ^3J = *22.7Hz*, ^3J= 2.5Hz); **^{13}C**: 20.6 (s, -CH_3 ax.), 21.9 (s, -CH_3 eq.), 32.2 (d, C-5, ^3J= 6.5Hz), 78.7 (d, C-4, C-6, ^2J= 9.0Hz), 108.3 (s, -*C*N), 127.4 (s, C-*orto),* 127.4 (s, *C-meta),* 129.3 (s, *C-para),* 133.2 (s, *C-ipso),* 141.2 (d, >*C*=N-, ^3J = 15.6Hz); **^{1}H** : 0.89 (s, 3H, -C*H*$_3$ ax.), 1.31 (s, 3H, -C*H*$_3$ eq.), 3.97 (dd, 2H, H-4e, H-6e, ^2J= 10.8Hz, ^3J = 22.7 Hz), 4.27 (dd, 2H, H-4a, H-6a, ^2J= 10.8Hz, ^3J = 2.5Hz), 7.00–8.00 (m, 5H, aromatic).

Rac-2-(α-Oximinophenylacetonitril)-2-thiono-5-methyl-1,3,2-dioxaphospholane (2).

2-Chloro-2-thiono-5-methyl-1,3,2-dioxaphospholane (8.6g 0.05mol), dissolved in dry acetone (50mL) was treated with stirring, at 40°C, with α-oximinophenylacetonitril sodium salt 8.4g(0.05mol). Then, similar procedure as for **1b** yielded the pure product (8.7g, 62% yield); m.p. = 113–5°C. *Anal. calcd. for* $C_{11}H_{11}N_2O_3PS$: C 46.80%; H 3.92%; N 9.92%; P 10.96%; found: C 46.67%; H 3.99%; N 10.14%; P 10.81%. *IR spectrum* (cm^{-1}): 2222 (ν_{CN}), 840, 640 ($\nu_{P=S}$), 900 (ν_{NO}). *Mass spectrum* (m/z, %): 282, (20), $[M]^+$; 252, (0.2), $[M\text{-}CH_2O]^{o+}$; 129, (91), $[C_6H_5(CN)C{=}N]^+$; 103, (14), $[C_6H_5\text{-}C{=}N]^+$;77, (100), $[C_6H_5]^+$. *NMR Spectra* ($CDCl_3$) **2-*cis* diastereomer: ^{31}P** (6, ppm; ^nJ,Hz): 81.30 (dddd, ^3J = 5.1Hz, ^3J = 10.1Hz, ^{3}J= 13.0Hz); **^{1}H:** 1.53 (d, 3H, -C*H*$_3$, ^3J = 5.6Hz), 4.14 (dddd, 1H, H-4t, ^3J = 5.6Hz, ^3J = 7.6Hz, ^3J = 8.6Hz, ^3J = 10.1Hz), 4.65 (ddd, 1H, H-5t, ^2J = 6.4Hz, ^3J = 8.6Hz, ^3J= 13.0Hz), 5.01 (ddd, 1H, H-5c, ^2J= 6.4Hz, ^3J = 7.6Hz, ^3J = 5.1Hz), 7.00–8.00 (m, 5H, aromatic); ***2-trans* diastereomer: ^{31}P** (δ, ppm; ^{n}J, Hz) : 81.65 (ddd, ^3J = 2.0Hz, ^3J = 4.4Hz, ^3J = 21.4Hz); **^{1}H**: 1.52 (d, 3H, -C*H*$_3$, ^3J= 6.1Hz), 4.19 (dddd, 1H, H-4c, ^3J = 6.1 Hz, ^3J = 1.0Hz, ^3J = 8.7Hz, ^3J = 2.0Hz), 4.60 (ddd, 1H, H-5t, ^2J= 6.4Hz, ^3J = 8.7Hz, ^3J = 21.4Hz), 4.97 (ddd, 1H, H-5c, ^2J = 6.4Hz, ^3J = 1.0Hz, ^3J = 4.4Hz), 7.00–8.00 (m, 5H, aromatic); **^{13}C (both diastereomers)**: 18.5 (d, -*C*H$_3$, ^3J = 6.3Hz), 19.7 (d, -CH_3, ^3J = 7.1Hz), 73.9 (s, C-5), 77.6 (s, C-4), 77.8 (s, C-4), 108.1 (s, -*C*N), 127.2 (s, C-*orto),*129.3 (s, C-*meta),* 129.4 (s, C-*para),* 133.3 (s, C-*ipso),* 140.4 (d, >*C*=N-, ^3J= 12.8Hz), 140.5 (d, >*C*=N-, ^3J = 12.6Hz).

bis-(α-Oximinophenylacetonitril)-cyclohexyl-phosphonate (3a)

Cyclohexylphosphonic acid dichloride (5.0g, 0.025mol) and α-oximinophenylacetonitril sodium salt (8.4g, 0.05mol), in dry diethyl ether (50mL) at 20°C, after 2hr. afforded the desired compound (4.2g, 40% yield); m.p. = 84–7°C. *Anal, calcd for* $C_{22}H_{21}N_4O_3P$: C 62.85%; H 5.03%; N 13.32%; P 7.36%; found: C 62.32%; H 4.98%; N 13.10%; P 7.22%. *IR spectrum*(cm^{-1}): 2220 (ν_{CN}), 1270 ($\nu_{P=O}$), 915 (ν_{N-O}). *Mass spectrum* (m/z, %): 420, (0.7), $[M]^+$; 275, (5), $[M\text{-}C_6H_5(CN)C{=}N\text{-}O]^+$; 129, (100), $[C_6H_5(CN)C{=}N]^+$; 77, (90), $[C_6H_5]^+$; 83, (18), $[C_6H_{11}]^+$. *NMR Spectra* ($CDCl_3$) ; **^{31}P** (δ, ppm; ^nJ, Hz): 39.90; **^{13}C** : 25.2 (d, C-4, ^4J = 4.6Hz), 25.3 (d, C-3, C-5, ^3J = 15.7Hz), 25.7 (d, C-2, C-6, ^2J= 16.5Hz), 34.4 (d, C-1, ^1J = 124.5Hz), 108.0 (s, -CN), 127.2 (s, C-*orto*), 127.5 (s, C-*meta*), 129.3 (s, C-*para*), 133.3 (s, C-*ipso*), 142.1 (d, >C=N-, ^3J= 13.3Hz) ; **^{1}H**: 1.30 – 2.55(m, 11H, cyclohexyl), 7.30 – 7.95 (m, 5H, phenyl).

bis-(α-Oximinophenylacetonitril)-cyclohexyl-thiophosphonate (3b)

Cyclohexylthiophosphonic acid dichloride (5.4g, 0.025mol) and a-oximinophenylacetonitril sodium salt (8.4g, 0.05mol), in diethyl ether (50mL) at 35°C, after 3hr. afforded the desired compound (4.6g, 42% yield); m.p. = 172–5°C. *Anal. calcd for* $C_{22}H_{21}N_4O_2PS$: C 60.53%; H 4.84%; N 12.83%; P 7.09%; found: C 60.78%; H 4.83%; N 12.84%; P 7.11%. *IR spectrum* (cm^{-1}): 2230 (ν_{CN}), 790, 640 ($\nu_{P=S}$), 910 (ν_{N-O}). *Mass spectrum* (m/z, %): 436, (1.4), $[M]^+$; 291, (2.8), $[M\text{-}C_6H_5(CN)C{=}N\text{-}O]^+$; 129, (90), $[C_6H_5(CN)C{=}N]^+$; 77, (100), $[C_6H_5]^+$; 83, (41), $[C_6H_{11}]^+$. *NMR Spectra* ($CDCl_3$) ; **^{31}P** (δ, ppm; ^nJ, Hz): 59.33; **^{13}C**: 25.5 (d, C-4, ^4J = 19.4Hz), 25.6 (s, C-3, C-5), 25.7 (d, C-2, C-6, ^2J = 18.3Hz), 40.1 (d, C-1, ^1J = 94.2Hz), 108.2 (s, -CN), 127.5 (s, C-*orto*), 127.6 (s, C-*meta*),129.3 (s, C-*para*), 133.1 (s, C-*ipso*), 141.4 (d, >C=N-, ^3J = 14.0Hz); **^{1}H**: 1.30 – 2.80(m, 11 H, cyclohexyl), 7.40 – 8.00 (m, 5H, phenyl).

bis-(α-Oximinophenylacetonitril)-ethoxyphosphate (4a)

Ethoxyphosphoric acid dichloride (4.1g, 0.025mol) and a-oximinophenylacetonitril sodium salt (8.4g, 0.05mol), in dry diethyl ether (50mL) at 20°C, after 2hr. afforded the desired compound (4.3g, 45% yield);

m.p. = 110–2°C. Anal. calcd. for $C_{18}H_{15}N_4O_4P$: C 56.54%; H 3.95%; N 14.65%; P 8.10%; found: C 56.52%; H 3.96%; N 14.67%; P 8.30%. *IR spectrum* (cm^{-1}): 2250 (ν_{CN}), 1305 ($\nu_{P=O}$), 980 (ν_{N-O}). *NMR Spectra* (DMSO-d_6); **^{31}P** (δ, ppm; ^nJ, Hz): 0.09; **^{13}C**: 17.0 (d, -CH_3, ^3J = 6.8Hz), 62.0 (d, -CH_2-, ^2J = 5.3Hz), 110.9 (s, -CN), 126.4 (s, *C-orto),* 130.1 (s, *C-meta),* 130.4 (s, >C=N-), 131.7 (s, *C-para),* 132.0 (s, *C-ipso);* **^{1}H**: 1.18 (t, 3H, -CH_3, ^3J = 7.0Hz), 3.80 (q, 2H, -CH_2-^3J = 7.0Hz, ^3J = 7.2Hz), 7.50 (m, 3H), 7.70 (m, 2H).

bis-(α-Oximinophenylacetonitril)-ethoxythiophosphate (4b)

Ethoxythiophosphoric acid dichloride (4.5g, 0.025mol) and α-oximinophenylacetonitril sodium salt (8.4g, 0.05mol), in dry diethyl ether (50mL) at 35°C, after 3hr. afforded the desired compound (4.5g, 45% yield); m.p. = 102–3°C. *Anal. calcd. for* $C_{18}H_{15}N_4O_3PS$: C 54.26%; H 3.79%; N 14.06%; P 7.77%; found: C 54.29%; H 3.91%; N 14.07%; P 7.86%. *IR spectrum*(cm^{-1}): 2240 (ν_{CN}), 820, 615 ($\nu_{P=S}$), 905 (ν_{N-O}). *Mass spectrum* (m/z, %): 398, (7), $[M]^+$; 366, (1), $[M-S]^+$; 129, (98), $[C_6H_5(CN)C=N]^+$; 77, (100), $[C_6H_5]^+$. *NMR Spectra* ($CDCl_3$) ; **^{31}P** (6, ppm; ^nJ, Hz): 68.31 (t, ^3J = 11.5Hz) ; **^{13}C**: 16.0 (d, -CH_3, ^3J = 6.1Hz), 67.7 (d, -CH_2-, ^2J = 6.0Hz), 108.0 (s, -CN), 127.3 (s, *C-orto),* 127.5 (s, *C-meta),* 129.3 (s, C-*para),*133.2 (s, C-*ipso);* 141.5 (d, >C=N-, ^3J = 16.6Hz); **^{1}H**: 1.39 (t, 3H, -CH_3, ^3J= 7.0Hz), 4.42 (qd, 2H, -CH_2-, ^3J= 7.0Hz,^3J= 11.5Hz).

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