Monatsh Chem 139, 747–752 (2008)
DOI 10.1007/s00706-007-0836-6
Printed in The Netherlands

**Monatshefte für Chemie
Chemical Monthly**

Ditolyldithiophosphato derivatives of phosphorus(III) and phosphorus(V)

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Received 27 September 2007; Accepted 24 October 2007; Published online 24 April 2008

Abstract *O*,*O′*-Ditolylphosphorodithioates of phosphorus(III), $[(o\text{-}, m\text{-}, \text{or } p\text{-}CH_3C_6H_4O)_2PS_2]_nPCl_{3-n}$, and phosphorus(V), $[(o\text{-}, m\text{-}, \text{or } p\text{-}CH_3C_6H_4O)_2PS_2]_nPOCl_{3-n}$, ($n = 1$, 2, and 3) were isolated as colorless viscous liquids by the reaction of PCl_3 and $POCl_3$ with sodium ditolylphosphorodithioate, $(o\text{-}, m\text{-}, \text{or } p\text{-}CH_3C_6H_4O)_2PS_2Na$, in 1:1, 1:2, and 1:3 molar ratios in toluene. These compounds were characterized by elemental analyses, molecular weight measurements, IR, and NMR (^1H, ^{31}P, and ^{13}C) spectroscopic studies, which indicated a less common monodentate linkage of dithiophosphate moieties in both phosphorus(III) and phosphorus(V) derivatives leading to a tetrahedral geometry around the phosphorus atom.

Keywords Cresyl; Ditolyl; Phosphorus compounds; Dithiophosphates.

Introduction

Dialkylphosphonates $[(RO)_2PO]^-$, dialkylthiophosphonates $[(RS)_2PO]^-$, dialkyldithiophosphates $[(OR)_2PS_2]^-$, and *O*,*O′*-alkylenedithiophosphates $[\overline{OGOP}S_2]^-$ have attracted wide attention in *academia* in particular for providing various bonding aspects with metals and metalloids [1–4]. A varieties of complexes have been reported in which the dithiophosphate ligands behave, normally, in a bidentate manner [5–11]. However, some compounds with less common monodentate linkages have also been described [12, 13]. It is pertinent to mention that these dithiophosphato derivatives find extensive applications in various fields, like agriculture [14, 15], industries [16, 17], and analytical studies [18, 19]. A literature survey revealed scanty information on *O*,*O′*-ditolyldithiophosphate ligands and their derivatives compared to dialkyl- and alkylenedithiophosphates [20–24]. In fact, no systematic study or review is available, in particular on the ditolyldithiophosphates. We have recently reported a convenient synthesis route of ditolyldithiophosphate ligands [25, 26]. These new ligands appeared to be potential chelating ligands to both metals and metalloids [27, 28]. In addition, some ditolyldithiophosphates have also found their use as rubber vulcanizers [29], aerofloats [30], polymerization catalysts [31], and in agriculture as acaricides or herbicides [32]. The compound $Sb[S_2P(O_2C_6H_4CH_3)_2]_3$ is reported as a passivation agent in petroleum refining [33]. In view of the above interesting facets of dithiophosphate chemistry and the utility of phosphorus compounds in biological activities [34, 35], it was considered to be of interest to extend the investigations on ditolyldithiophosphate derivatives particularly having more than one phosphorus moieties in the molecule. Thus, we report herein the synthesis and characterization of phosphorus(III) and phosphorus(V) derivatives of ditolyldithiophosphates by reacting sodium ditolylphosphorodithioates with PCl_3 and $POCl_3$ in different stoichiometries.

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Results and discussion

Reactions of sodium *O*,*O*′-(*o*-, *m*-, or *p*-ditolyl)phosphorodithioate or (*o*-, *m*-, or *p*-$CH_3C_6H_4O)_2PS_2Na$ (**1a**–**1c**), with phosphorus trichloride, PCl_3 (**2a**), and phosphorus oxychloride, $POCl_3$ (**2b**), in 1:1, 2:1, and 3:1 molar ratio in refluxing toluene resulted in the formation of (*o*-, *m*-, or *p*-ditolyl) dithiophosphato derivatives of phosphorus(III), $[(CH_3C_6H_4O)_2PS_2]_n$-PCl_{3-n} (**3a**–**3i**), and of phosphorus(V), $[(CH_3C_6H_4O)_2PS_2]_nPOCl_{3-n}$, (**4a**–**4i**), ($n = 1$, 2 or 3) as colorless viscous liquids in 85–92% yield (Scheme 1).

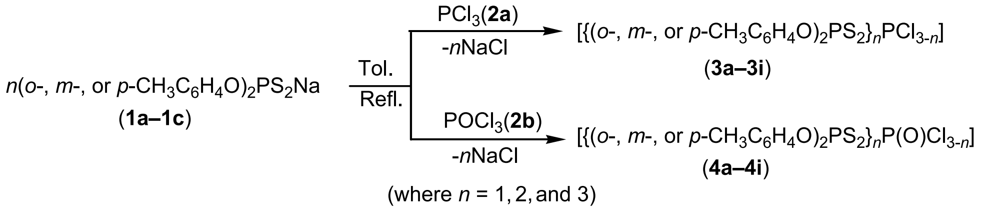
The syntheses of the compounds have been achieved by cleavage of the phosphorus-chlorine bond present in phosphorus trichloride and phosphorus oxychloride. The removal of chloride ion might take place as a consequence of a nucleophilic displacement with the dithiophosphate moiety as illustrated in Scheme 2.

The elemental analyses of these compounds (C, H, Cl, and S) were found to be consistent with their molecular formula. These derivatives are non-volatile, soluble in common organic solvents *viz.* toluene, benzene, chloroform and methylenechloride, but insoluble in *n*-hexane. Although these compounds appeared to be moisture sensitive, they can be stored unchanged for a long time under dry conditions. The monomeric nature of these compounds was confirmed by the molecular weight determination of few compounds.

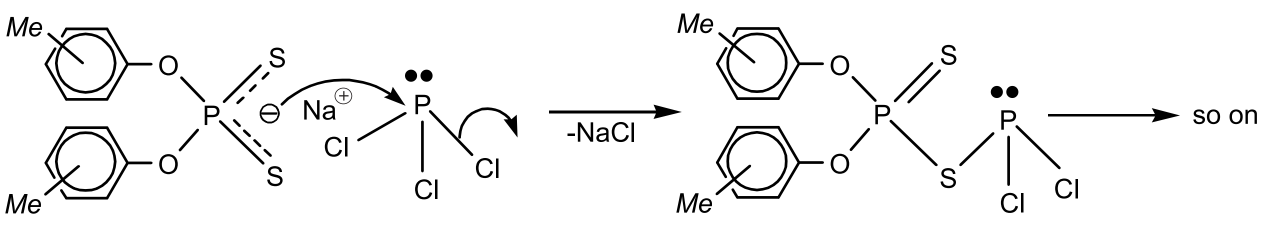
IR spectra of these derivatives have been interpreted on comparative basis with literature reports [20–23, 36, 37]. Appearance of a new absorption band of medium intensity in the range $\bar{\nu} = 652–552\,\mathrm{cm}^{-1}$, which is overlapped slightly with the $\bar{\nu}$P–S vibration of the dithiophosphate moiety, may be attributed to the formation of new $\bar{\nu}$P–S chemical linkage. The absorption bands of strong intensity present in the regions $\bar{\nu} = 1185–1139\,\mathrm{cm}^{-1}$ and $\bar{\nu} = 959–913\,\mathrm{cm}^{-1}$ are tentatively assigned for $\bar{\nu}$(P)–O–C and $\bar{\nu}$P–O–(C) vibrations. The $\bar{\nu}$P=S vibrations of the dithiophosphate moiety occurred in the region $\bar{\nu} = 782–655\,\mathrm{cm}^{-1}$. Aromatic $\bar{\nu}$C–H vibrations were observed in their characteristic range of $\bar{\nu} = 2983–2921\,\mathrm{cm}^{-1}$ for all compounds. The phosphoryl ($\bar{\nu}$P=O) absorption bands in the derivatives **4a**–**4i** appeared in the range of $\bar{\nu} = 1340–1294\,\mathrm{cm}^{-1}$. Bands at $\bar{\nu} = 627–505\,\mathrm{cm}^{-1}$ have been assigned to the $\bar{\nu}$P–Cl vibrations in the compounds **3a**–**3f** and **4a**–**4f**. The disappearance of the band for $\bar{\nu}$P–Cl absorption in the spectra of the compounds **3g**–**3i** and **4g**–**4i** is suggestive of replacement of all three chlorine atoms attached to PCl_3 and $POCl_3$ by the dithiophosphate ligand.

The ^{1}H NMR spectra of these compounds display a singlet for the methyl and a multiplet for tolyl ring protons at $\delta = 2.3$ ppm and $\delta = 7.0–8.2$ ppm. These chemical shift values did not indicate any shift comparable to the parent dithiophosphate ligands.

The ^{31}P NMR chemical shifts clearly indicated two different types of chemically non-equivalent phosphorus atom. The trivalent phosphorus atom in the compounds **3a**–**3i** appeared in the region $\delta = 193.6–197.5$ ppm, which show the shielding of phosphorus atom to the extent of about $\delta = 24–28$ ppm



Scheme 1



Scheme 2

from its position in free phosphorus trichloride (^{31}P = 221 ppm). The phosphorus atom of phosphoryl (P=O) group in the compounds **4a**–**4i** appeared as singlet in the region $\delta = 6.5$–13.7 ppm, which is deshielded compared to its position at $\delta = 1.9$ ppm in free phosphorus oxychloride. The chemical shift of the phosphorus atom of dithiophosphate moiety was found as doublet in the range $\delta = 80.1$–88.2 ppm. Perhaps, this is due to the asymmetrical nature of the phosphorus nuclei in the molecule and also due to monodentate mode of bonding of dithiophosphate ligand towards the other phosphorus atom.

In the ^{13}C NMR spectra of some representative compounds (**3a**, **3f**, **3h**, **4a**, **4e**, and **4i**), the chemical shift for the $-CH_3$ carbon attached to the tolyl rings were found in the region $\delta = 17.4$–17.5 ppm. The chemical shifts for *ortho-*, *meta-*, and *para-* carbons were found in the region $\delta = 121.7$–130.4, 124.4–129.4 and 126.4–131.3 ppm. The shifts for C–O carbon of *O*,*O*′-(*meta-* or *para*-ditolyl)dithiophosphato derivatives of P(III) (**3f** and **3h**) and P(V) (**4e** and **4i**) were found in the region 154.3–154.7 ppm. This is indicative of intramolecular hydrogen bonding between a proton attached to one of the *ortho* carbons of one tolyl ring and the oxygen atom O–(C) of the other tolyl ring. However, the shift for C–O carbon of *O*,*O*′-(*ortho*-ditolyl)dithiophosphato derivatives (**3a**, **4a**) was observed in the normal range $\delta =$ 150.8–151.1 ppm, showing the absence of intramolecular hydrogen bonding. The presence of hydrogen bonding in *O*,*O*′-(*meta-* or *para*-ditolyl)dithiophosphato derivatives is also confirmed by chemical shift for the C–(CH_3) carbon ($\delta = 115.1$–115.8 ppm) compared to the shift in *O*,*O*′-(*ortho*-ditolyl)dithiophosphato derivative, which lies in the normal region ($\delta = 122.0$–122.2 ppm). Perhaps, the low field swing for the chemical shift due to the C–(CH_3) carbon of *O*,*O*′-(*meta-* or *para*-ditolyl)dithiophosphato derivatives is owing to hydrogen bonding between proton attached to the (*ortho*) carbon of one tolyl ring with the oxygen atom of other tolyl ring.

Structural features

It was not possible to assign precisely the structure of these compounds since these compounds are viscous liquids and can not be crystallized. However, on the basis of elemental analyses, molecular weight determination, and spectroscopic studies like IR and NMR (^{1}H, ^{13}C, and ^{31}P) and in conjunction with literature reports [20–23, 36, 37], a probable geometry around the phosphorus(III) and phosphorus(V) in different coordination spheres may tentatively be assigned to these compounds. The ^{31}P spectra of the compounds (**3a**–**3i**) display a doublet, which is suggestive of a monodentate linkage of the dithiophosphate ligand, hence only one sulfur atom of the dithiophosphate ligand might be attached to the phosphorus(III) atom leaving another sulfur atom non-bonded. Therefore, a distorted tetrahedral geometry is assigned around the phosphorus(III) atom in the compounds **3a**–**3i** in which the fourth position is occupied by a lone pair of electrons (Fig. 1). Considering the similar aspects, the compounds **4a**–**4i** might have akin geometrical arrangement around the phosphorus(V) atom of $POCl_3$ except that a lone pair of electrons on the phosphorus(III) is replaced by a doubly bonded oxygen atom (Fig. 2).

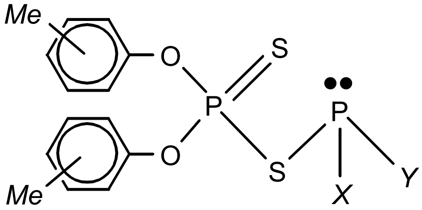


Fig. 1 *X* and *Y* = Cl for **3a**–**3c**; *X* = **1a**–**1c** and *Y* = Cl for **3d**–**3f**; *X* and *Y* = **1a**–**1c** for **3g**–**3i**

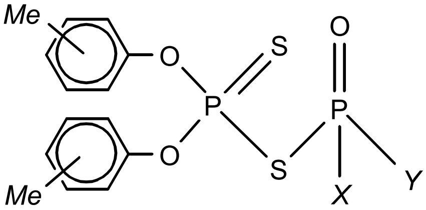


Fig. 2 *X* and *Y* = Cl for **4a**–**4c**; *X* = **1a**–**1c** and *Y* = Cl for **4d**–**4f**; *X* and *Y* = **1a**–**1c** for **4g**–**4i**

Experimental

Moisture was carefully excluded throughout the experimental manipulations by using standard *Schlenk*'s technique. Toluene and benzene were freshly dried by refluxing over sodium, followed by distillation. Sulfur was estimated gravimetrically as barium sulfate (*Messenger*'s method) and chlorine was estimated volumetrically by *Volhard*'s method. Elemental analyses were conducted using a Leco CHNS-932 analyzer; their results were well in accord with the calculated values. Molecular weights were determined by cryoscopic method in freezing benzene. IR spectra were recorded in nujol mulls in the range of $\bar{\nu} = 4000$–200 cm^{-1} on a Perkin Elmer-557 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Brucker DRX 300 (120 MHz) using *TMS* as external reference. The ^{31}P NMR spectra were recorded in $CDCl_3$ using H_3PO_4 (85%) as external reference on a Brucker DRX 300 (120 MHz).

(Bis(o-tolyloxy)phosphorothioylthio)phosphorus(III)chloride (**3a**, $C_{14}H_{14}O_2PS_2Cl_2$)

To a toluene suspension ($\sim$35 cm^3) of sodium *O,O′*-(*o*-ditolyl)phosphorodithioate, 1.12 g (*o*-$CH_3C_6H_4O)_2PS_2Na$ (**1a**) (0.33 mmol) was added dropwise a toluene solution ($\sim$15 cm^3) of 0.46 g PCl_3 (**2a**) (0.34 mmol) by using a dropping funnel with constant stirring at room temperature. The contents were refluxed for $\sim$3 h during which a white precipitate of NaCl was formed. The reaction was allowed to reach room temperature, then filtered through an alkoxy funnel fitted with a G-4 sintered disc followed by evaporation of excess of solvent from the filtrate under reduced pressure. The product was finally dried *in vacuo* for 3 h, which yielded [(*o*-$CH_3C_6H_4O)_2PS_2PCl_2$] (**3a**) as colorless viscous liquid. Yield: 1.25 g (90%); M.W. calcd. for $C_{14}H_{14}O_2PS_2Cl_2$: 411.23, found: 398.72; IR (nujol): $\bar{\nu}$ = 2981b, 1163s, 926s, 760m, 595m, 525w cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 6H, CH_3 of cresol), 7.0–7.9 (m, 8H, C_6H_4) ppm; ^{13}C NMR (120 MHz, $CDCl_3$): δ = 17.4 (s, CH_3), 150.9–151.1 (m, C–O), 122.0 (d, C–CH_3), 123.2–123.7 (m, C-*ortho*), 124.5–125.7 (m, C-*meta*), 126.8–131.3 (m, C-*para*) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 80.1 (d, dithio), 195.0 (s, PCl_2) ppm.

(Bis(m-tolyloxy)phosphorothioylthio)phosphorus(III)-chloride (**3b**, $C_{14}H_{14}O_2PS_2Cl_2$)

According to the procedure described for **3a**, 1.06 g of (*m*-$CH_3C_6H_4O)_2PS_2Na$ (**1b**) (0.31 mmol) and 0.43 g of PCl_3 (**2a**) (0.31 mmol) were used to give **3b** as a colorless viscous liquid. Yield: 1.21 g (92%); M.W. calcd. for $C_{14}H_{14}O_2PS_2Cl_2$: 411.23, found: 401.14; IR (nujol): $\bar{\nu}$ = 2922b, 1146s, 959s, 782m, 596m, 528w cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 6H, CH_3 of cresol), 7.1–8.0 (m, 8H, C_6H_4) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 80.6 (d, dithio), 197.5 (s, PCl_2) ppm.

(Bis(p-tolyloxy)phosphorothioylthio)phosphorus(III)chloride (**3c**, $C_{14}H_{14}O_2PS_2Cl_2$)

According to the procedure described for **3a**, 1.28 g of (*p*-$CH_3C_6H_4O)_2PS_2Na$ (**1c**) (0.38 mmol) and 0.52 g of PCl_3 (0.38 mmol) (**2a**) were used to give **3c** as a colorless viscous liquid. Yield: 1.43 g (90%); IR (nujol): $\bar{\nu}$ = 2981b, 1162s, 922s, 725m, 652m, 511w cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 6H, CH_3 of cresol), 7.0–8.0 (m, 8H, C_6H_4) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 81.2 (d, dithio), 197.7 (s, PCl_2) ppm.

Bis(bis(o-tolyloxy)phosphorothioylthio)phosphorus(III)-chloride (**3d**, $C_{28}H_{28}O_4P_3S_4Cl$)

According to the procedure described for **3a**, 1.31 g of (*o*-$CH_3C_6H_4O)_2PS_2Na$ (**1a**) (0.39 mmol) and 0.27 g of PCl_3 (**2a**) (0.19 mmol) were used to give **3d** as a colorless viscous liquid. Yield: 2.35 g (87%); IR (nujol): $\bar{\nu}$ = 2982b, 1162s, 926s, 760m, 601m, 523w cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 12H, CH_3 of cresol), 7.0–7.9 (m, 16H, C_6H_4) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 82.3 (d, dithio), 193.6 (s, PCl) ppm.

Bis(bis(m-tolyloxy)phosphorothioylthio)phosphorus(III)-chloride (**3e**, $C_{28}H_{28}O_4P_3S_4Cl$)

According to the procedure described for **3a**, 1.16 g of (*m*-$CH_3C_6H_4O)_2PS_2Na$ (**1b**) (0.35 mmol) and 0.24 g of PCl_3 (**2a**) (0.17 mmol) were used to give **3e** as a colorless viscous liquid. Yield: 2.41 g (88%); M.W. calcd. for $C_{28}H_{28}O_4P_3S_4Cl$: 685.13, found: 662.12; IR (nujol): $\bar{\nu}$ = 2983b, 1142s, 948s, 687m, 598m, 541w cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 12H, CH_3 of cresol), 7.1–8.0 (m, 16H, C_6H_4) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 82.6 (d, dithio), 193.8 (s, PCl) ppm.

Bis(bis(p-tolyloxy)phosphorothioylthio)phosphorus(III)-chloride (**3f**, $C_{28}H_{28}O_4P_3S_4Cl$)

According to the procedure described for **3a**, 1.89 g of (*p*-$CH_3C_6H_4O)_2PS_2Na$ (**1c**) (0.56 mmol) and 0.39 g of PCl_3 (**2a**) (0.28 mmol) were used to give **3f** as a colorless viscous liquid. Yield: 3.46 g (89%); M.W. calcd. for $C_{28}H_{28}O_4P_3S_4Cl$: 685.13, found: 696.42; IR (nujol): $\bar{\nu}$ = 2923b, 1159s, 918s, 720m, 651m, 505w cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 12H, CH_3 of cresol), 7.0–8.0 (m, 16H, C_6H_4) ppm; ^{13}C NMR (120 MHz, $CDCl_3$): δ = 17.4 (s, CH_3), 154.3 (m, C–O), 115.2 (d, C–CH_3), 126.6–130.4 (m, C-*ortho*), 127.2–129.4 (m, C-*meta*); 126.6–129.6 (m, C-*para*) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 83.1 (d, dithio), 196.2 (s, PCl) ppm.

Tris(bis(o-tolyloxy)phosphorothioylthio)phosphorus(III) (**3g**, $C_{42}H_{42}O_6P_4S_6$)

According to the procedure described for **3a**, 2.26 g of (*o*-$CH_3C_6H_4O)_2PS_2Na$ (**1a**) (0.68 mmol) and 0.37 g of PCl_3 (**2a**) (0.22 mmol) were used to give **3g** as a colorless viscous liquid. Yield: 5.53 g (85%); IR (nujol): $\bar{\nu}$ = 2976b, 1170s, 928s, 758m, 597m cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 18H, CH_3 of cresol), 7.0–7.9 (m, 24H, C_6H_4) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 84.9 (d, dithio), 195.2 (s, P of PCl_3) ppm.

Tris(bis(m-tolyloxy)phosphorothioylthio)phosphorus(III) (**3h**, $C_{42}H_{42}O_6P_4S_6$)

According to the procedure described for **3a**, 2.75 g of (*m*-$CH_3C_6H_4O)_2PS_2Na$ (**1b**) (0.82 mmol) and 0.37 g of PCl_3 (**2a**) (0.27 mmol) were used to give **3h** as a colorless viscous liquid. Yield: 6.96 g (88%); IR (nujol): $\bar{\nu}$ = 2926b, 1154s, 946s, 720m, 600m cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 18H, CH_3 of cresol), 7.0–8.1 (m, 24H, C_6H_4) ppm; ^{13}C NMR (120 MHz, $CDCl_3$): δ = 17.5 (s, CH_3), 154.6 (m, C–O), 115.1 (d, C–CH_3), 127.2–130.1 (m, C-*ortho*), 126.3–129.2 (m, C-*meta*), 127.9–130.2 (m, C-*para*) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 86.8 (d, dithio), 196.8 (s, P of PCl_3) ppm.

Tris(bis(p-tolyloxy)phosphorothioylthio)phosphorus(III) (**3i**, $C_{42}H_{42}O_6P_4S_6$)

According to the procedure described for **3a**, 2.53 g of (*p*-$CH_3C_6H_4O)_2PS_2Na$ (**1c**) (0.76 mmol) and 0.34 g of PCl_3 (**2a**) (0.25 mmol) were used to give **3i** as a colorless viscous liquid.

Yield: 6.05 g (83%); M.W. calcd. for $C_{42}H_{42}O_6P_4S_6$: 959.04, found: 984.17; IR (nujol): $\bar{\nu}$ = 2923b, 1160s, 918s, 726m, 652m cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 18H, CH_3 of cresol), 7.0–8.0 (m, 24H, C_6H_4) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 85.1 (d, dithio), 195.5 (s, P of PCl_3) ppm.

(Bis(o-tolyloxy)phosphorothioylthio)(oxo)phosphorus(V)-chloride (**4a**, $C_{14}H_{14}O_3P_2S_2Cl_2$)

According to the procedure described for **3a**, 0.95 g of (*o*-$CH_3C_6H_4O)_2PS_2Na$ (**1a**) (0.28 mmol) and 0.43 g of $POCl_3$ (**2b**) (0.28 mmol) were used to give **4a** as a colorless viscous liquid. Yield: 1.12 g (92%); IR (nujol): $\bar{\nu}$ = 2967b, 1147s, 936s, 657m, 552m, 1328m, 620w cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 6H, CH_3 of cresol), 7.8–8.2 (m, 8H, C_6H_4) ppm; ^{13}C NMR (120 MHz, $CDCl_3$): δ = 17.5 (s, CH_3), 150.9–151.0 (m, C–O), 122.2 (d, C–CH_3), 121.7–130.0 (m, C-*ortho*), 124.4–125.9 (m, C-*meta*), 126.4–127.1 (m, C-*para*) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 82.0 (d, dithio), 6.5 (s, $POCl_2$) ppm.

(Bis(m-tolyloxy)phosphorothioylthio)(oxo)phosphorus(V)-chloride (**4b**, $C_{14}H_{14}O_3P_2S_2Cl_2$)

According to the procedure described for **3a**, 1.13 g of (*m*-$CH_3C_6H_4O)_2PS_2Na$ (**1b**) (0.34 mmol) and 0.52 g of $POCl_3$ (**2b**) (0.34 mmol) were used to give **4a** as a colorless viscous liquid. Yield: 1.30 g (90%); M.W. calcd. for $C_{14}H_{14}O_3P_2S_2Cl_2$: 427.23, found: 406.14; IR (nujol): $\bar{\nu}$ = 2972b, 1139s, 938s, 655m, 561m, 1332m, 625w cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 6H, CH_3 of cresol), 7.7–8.0 (m, 8H, C_6H_4) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 82.7 (d, dithio), 6.7 (s, $POCl_2$) ppm.

(Bis(p-tolyloxy)phosphorothioylthio)(oxo)phosphorus(V)-chloride (**4c**, $C_{14}H_{14}O_3P_2S_2Cl_2$)

According to the procedure described for **3a**, 1.07 g of (*p*-$CH_3C_6H_4O)_2PS_2Na$ (**1c**) (0.32 mmol) and 0.49 g of $POCl_3$ (**2b**) (0.32 mmol) were used to give **4c** as a colorless viscous liquid. Yield: 1.26 g (92%); IR (nujol): $\bar{\nu}$ = 2970b, 1143s, 942s, 670m, 559m, 1340m, 627w cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 6H, CH_3 of cresol), 7.8–8.1 (m, 8H, C_6H_4) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 82.3 (d, dithio), 6.4 (s, $POCl_2$) ppm.

Bis(bis(o-tolyloxy)phosphorothioylthio)(oxo)phosphorus(V)-chloride (**4d**, $C_{28}H_{28}O_5P_3S_4Cl$)

According to the procedure described for **3a**, 1.86 g of (*o*-$CH_3C_6H_4O)_2PS_2Na$ (**1a**) (0.56 mmol) and 0.43 g of $POCl_3$ (**2b**) (0.28 mmol) were used to give **4d** as a colorless viscous liquid. Yield: 3.26 g (83%); M.W. calcd. for $C_{28}H_{28}O_5P_3S_4Cl$: 701.13, found: 719.86; IR (nujol): $\bar{\nu}$ = 2956b, 1156s, 918s, 666m, 555m, 1297m, 617w cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 12H, CH_3 of cresol), 7.8–8.2 (m, 16H, C_6H_4) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 83.5 (d, dithio), 13.7 (s, POCl) ppm.

Bis(bis(m-tolyloxy)phosphorothioylthio)(oxo)phosphorus(V)-chloride (**4e**, $C_{28}H_{28}O_5P_3S_4Cl$)

According to the procedure described for **3a**, 1.22 g of (*m*-$CH_3C_6H_4O)_2PS_2Na$ (**1b**) (0.36 mmol) and 0.28 g of $POCl_3$ (**2b**) (0.18 mmol) were used to give **4e** as a colorless viscous liquid. Yield: 2.21 g (86%); IR (nujol): $\bar{\nu}$ = 2960b, 1153s, 922, 658m, 560m, 1300m, 608w cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 12H, CH_3 of cresol), 7.7–8.0 (m, 16H, C_6H_4) ppm; ^{13}C NMR (120 MHz, $CDCl_3$): δ = 17.4 (s, CH_3), 154.7 (m, C–O), 115.6 (d, C–CH_3), 123.2–124.1 (m, C-*ortho*), 124.7–125.6 (m, C-*meta*), 128.2–127.7 (m, C-*para*) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 87.6 (d, dithio), 13.4 (s, POCl) ppm.

Bis(bis(p-tolyloxy)phosphorothioylthio)(oxo)phosphorus(V)-chloride (**4f**, $C_{28}H_{28}O_5P_3S_4Cl$)

According to the procedure described for **3a**, 1.01 g of (*p*-$CH_3C_6H_4O)_2PS_2Na$ (**1c**) (0.30 mmol) and 0.23 g of $POCl_3$ (**2b**) (0.15 mmol) were used to give **4f** as a colorless viscous liquid. Yield: 1.81 g (85%); IR (nujol): $\bar{\nu}$ = 2958b, 1154s, 924s, 662m, 562m, 1294m, 612w cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 12H, CH_3 of cresol), 7.8–8.1 (m, 16H, C_6H_4) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 88.2 (d, dithio), 13.6 (s, POCl) ppm.

Tris(bis(o-tolyloxy)phosphorothioylthio)(oxo)phosphorus(V) (**4g**, $C_{42}H_{42}O_7P_4S_6$)

According to the procedure described for **3a**, 1.42 g of (*o*-$CH_3C_6H_4O)_2PS_2Na$ (**1a**) (0.42 mmol) and 0.22 g of $POCl_3$ (**2b**) (0.14 mmol) were used to give **4g** as a colorless viscous liquid. Yield: 3.63 g (87%); M.W. calcd. for $C_{42}H_{42}O_7P_4S_6$: 975.04, found: 993.28; IR (nujol): $\bar{\nu}$ = 2963b, 1148s, 913s, 665m, 560m, 1318m cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 18H, CH_3 of cresol), 7.8–8.2 (m, 24H, C_6H_4) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 87.3 (d, dithio), 13.5 (s, PO) ppm.

Tris(bis(m-tolyloxy)phosphorothioylthio)(oxo)phosphorus(V) (**4h**, $C_{42}H_{42}O_7P_4S_6$)

According to the procedure described for **3a**, 1.51 g of (*m*-$CH_3C_6H_4O)_2PS_2Na$ (**1b**) (0.45 mmol) and 0.23 g of $POCl_3$ (**2b**) (0.15 mmol) were used to give **4h** as a colorless viscous liquid. Yield: 3.95 g (89%); M.W. calcd. for $C_{42}H_{42}O_7P_4S_6$: 975.04, found: 961.03; IR (nujol): $\bar{\nu}$ = 2971b, 1152s, 918s, 668m, 565m, 1320m cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 18H, CH_3 of cresol), 7.7–8.0 (m, 24H, C_6H_4) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 87.1 (d, dithio), 13.4 (s, PO) ppm.

Tris(bis(p-tolyloxy)phosphorothioylthio)(oxo)phosphorus(V) (**4i**, $C_{42}H_{42}O_7P_4S_6$)

According to the procedure described for **3a**, 1.97 g of (*p*-$CH_3C_6H_4O)_2PS_2Na$ (**1c**) (0.59 mmol) and 0.30 g of $POCl_3$ (**2b**) (0.19 mmol) were used to give **4i** as a colorless viscous liquid. Yield: 5.27 g (91%); IR (nujol): $\bar{\nu}$ = 2962b, 1150s, 917s, 670m, 562m, 1326m cm^{-1}; ^{1}H NMR (120 MHz, $CDCl_3$): δ = 2.3 (s, 18H, CH_3 of cresol), 7.8–8.1 (m, 24H, C_6H_4) ppm; ^{13}C NMR (120 MHz, $CDCl_3$): δ = 17.5 (s, CH_3), 154.5 (m, C–O), 115.8 (d, C–CH_3), 122.6–123.1 (m, C-*ortho*), 125.8–126.5 (m, C-*meta*), 127.7–128.4 (m, C-*para*) ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 87.6 (d, dithio), 13.6 (s, PO) ppm.

Acknowledgement

We are grateful to Central Drug Research Institute, Lucknow for providing spectral facilities.

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