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ORIGINAL PAPER

O-Tolyl/benzyl dithiocarbonates of phosphorus(III) and (V): syntheses and characterization

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Abstract *O*-Tolyl/benzyl dithiocarbonates, $ROCS_2Na$ ($R = o$-, m-, or p-$CH_3C_6H_4$–, and –$CH_2C_6H_5$), were synthesized and characterized. These new ligands reacted with $PCl_3/POCl_3$ in refluxing toluene which resulted in the formation of phosphorus(III) and phosphorus(V) tolyl/benzyl dithiocarbonates corresponding to $[(ROCS_2)_nPCl_{3-n}]$ and $[(ROCS_2)_nPOCl_{3-n}]$ ($R = o$-, m-, or p-$CH_3C_6H_4$–, and –$CH_2C_6H_5$; $n = 1, 2, 3$). These pale yellow liquid compounds were characterized by IR, mass, and NMR (^1H, ^{13}C, and ^{31}P) spectral studies, which suggest the dithiocarbonate ligands bind in a monodentate mode leading to P–S–C linkages in these derivatives.

Keywords Dithiocarbonate · Phosphorus compounds · Total synthesis · Spectroscopy

Introduction

O-Alkyldithiocarbonates ($ROCS_2^-$) [1, 2] are an important class of 1,1-dithiolate ligands along with dithiocarbamates ($R_2N–CS_2^-$) [3, 4], dithiocarboxylates (RCS_2^-), dithiophosphates ($(RO)_2PS_2^-$) [5–8], and other related phosphor-1,1-dithiolate ligands. Metallic derivatives of $ROCS_2^-$ ligands have been known since 1815, when these were first prepared by Zeise, who also termed them xanthates, a name derived from the Greek xanthos (yellow), owing to the yellow color of lead xanthates [9]. Their applications to the vulcanization of rubber, as fungicides, and as flotation agents in metallurgy have been described in the literature [10]. The synthetic and structural chemistry of xanthates witnessed increased attention through the pioneering work of Winter, Hoskins, and others [11–14]. Subsequently, extensive structural analyses were performed by Haiduc and Tiekink, which showed that these ligands can coordinate to metal atoms in a monodentate, isobidentate, or anisobidentate fashion. Metal xanthates are extensively used as pharmaceuticals [15], fungicides [16], pesticides [17], corrosion inhibitors [18], agricultural reagents [19], and quite recently in therapy for HIV infections [20]. The last two decades have witnessed a tremendous development of new radical reactions designed for organic synthesis [21, 22]. Xanthates are not only convenient precursors for transforming an alcohol into the corresponding alkane [23], but also are extremely efficient and versatile sources of radicals, e.g., in carbon–carbon bond forming reactions [24].

Phosphorus is a vital component of biological cytoplasm and is also an essential element for plant growth. Phosphorus derivatives are used in numerous applications, e.g., water treatment [25], agrochemical products [26, 27], fire protection [28], oil field drilling [29, 30], fine chemicals [31, 32], and plastic additives [33, 34]. Although there are some restrictions on the use of certain organophosphorus compounds in developed countries, these compounds are still widely employed in several developing countries owing to their effectiveness in plague control [35]. Certain organophosphorus compounds containing substituted *p*-toluidine moieties were prepared for evaluation as cancer chemotherapeutic agents [36].

Surprisingly, in spite of years of chemistry of the extensive and long-term use of alkyl xanthates as ligands [37–44], structural and spectroscopic characterization has been rather limited with regard to the aryl xanthates [45, 46]. Fackler et al. [45], however, reported the synthesis of thallium aryl

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xanthates which in turn were used for the metathetical synthesis of other metal derivatives. We report herein the synthesis and characterization of *O*-tolyl/benzyl dithiocarbonates of phosphorus(III) and (V) by the reaction of sodium *O*-tolyl/benzyl dithiocarbonates with PCl_3 and $POCl_3$.

Results and discussion

Alkyl xanthates are usually synthesized by mixing KOH/NaOH with alcohols (excess) to produce ROK/RONa followed by insertion of CS_2 [9]. We, however, synthesized tolyl/benzyl xanthates by using sodium metal and toluene as solvent instead of KOH/NaOH and the parent alcohol as solvent. Reaction of sodium metal with *ortho*-, *meta*-, and *para*-cresols (*o*-, *m*-, and *p*-$CH_3C_6H_4OH$) and benzyl alcohol ($C_6H_5CH_2OH$) in 1:1 stoichiometric ratio in refluxing toluene resulted in the formation of sodium methylphenolates (*o*-, *m*-, and *p*-$CH_3C_6H_4ONa$) and sodium phenylmethanolate ($C_6H_5CH_2ONa$) as creamish viscous pasty masses. Addition of an equimolar amount of CS_2 to these at 0–5 °C forms the corresponding sodium salt of (*o*-, *m*-, and *p*-cresyl/benzyl) dithiocarbonates as a pale yellow solid (Scheme 1).

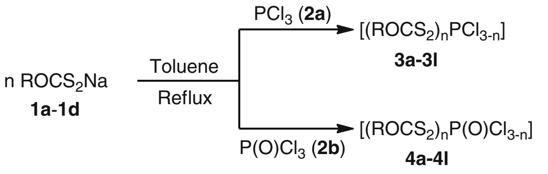
These sodium salts appear to be hygroscopic in nature, soluble in methanol, ethanol, acetone, and tetrahydrofuran, insoluble in most hydrocarbon solvents, and sparingly soluble in chloroform and dichloromethane. These compounds are non-volatile even under reduced pressure and tend to decompose on heating. Reactions of phosphorus trichloride, PCl_3 (**2a**), and phosphorus oxychloride, $POCl_3$ (**2b**), with the sodium salt of (*o*-, *m*-, and *p*-cresyl/benzyl) dithiocarbonates, (*o*-, *m*-, and *p*-$CH_3C_6H_4OCS_2$)Na/($C_6H_5CH_2OCS_2$)Na (**1a**–**1d**), in 1:1, 1:2, and 1:3 molar ratios were carried out in refluxing toluene which resulted in compounds $[(ROCS_2)_nPCl_{3-n}]$ **3a**–**3l** and $[(ROCS_2)_nPOCl_{3-n}]$ **4a**–**4l** (R = *o*-, *m*-, and *p*-$CH_3C_6H_4$– and –$CH_2C_6H_5$; $n = 1, 2, 3$) as pale yellow viscous liquids in 80–90% yield (Scheme 2).

The compounds were isolated by evaporation under reduced pressure. These derivatives are non-volatile, monomeric, and soluble in common organic solvents. All these compounds are obtained in sufficient purity as revealed by spectral studies.

It is observed that the reactions of phosphorus oxychloride are less facile than the corresponding reactions of phosphorus trichloride and needed longer reaction times (10–12 h at reflux) to ensure their completion. It is assumed that this might be due to the high electronegativity of oxygen and steric bulk of $POCl_3$, which thereby makes the nucleophilic displacement of chloride ions from the phosphorus oxychloride moiety difficult compared with that from phosphorus trichloride.

R = *o*-, *m*-, or *p*-$CH_3C_6H_4$- (**1a-1c**), and $C_6H_5CH_2$- (**1d**)

Scheme 1



R = *o*-, *m*-, or *p*-$CH_3C_6H_4$- (**3a-3c**, **3e-3g**, **3i-3k**, **4a-4c**, **4e-4g**, and **4i-4k**); and $C_6H_5CH_2$- (**3d**, **3h**, **3l**, **4d**, **4h**, and **4l**)

Scheme 2

IR spectra

The characteristic stretching bands in the IR spectra (4,000–400 cm^{-1}) were assigned by comparison with literature data [37–49]. The IR spectra show the characteristic sharp band for ν (C–O–C) and broad band for ν (C=C) (tolyl and benzyl ring stretching) in the range 1,043–1,015 and 1,607–1,581 cm^{-1}, respectively. The strong frequency bands for ν (C=S) and (C–S) appeared in the range 1,194–1,160 and 945–920 cm^{-1}; the separation between these bands is quite large (240–150 cm^{-1}) as is usually observed in the case of monodentate linkages [50]. Also the strong band due to C=S stretching vibrations present in the spectra of sodium salts of tolyl/benzyl dithicarbonates **1a**–**1d** in the region 1,145–1,140 cm^{-1} is shifted towards higher frequency in the spectra of compounds **3a**–**3l** and **4a**–**4l** and is present in the range 1,194–1,160 cm^{-1}. This shifting indicates, most probably, a monodentate chelation of the dithiocarbonate moiety with phosphorus. The IR spectra of compounds **3a**–**3l** and **4a**–**4l** show the appearance of a new band of medium intensity for ν (P–S) in the region 564–520 cm^{-1}, indicating the formation of a bond between the phosphorus atom and dithiocarbonate moiety. The phosphoryl ν (P=O) absorption band in the derivatives **4a**–**4l** appeared in the region 1,290–1,262 cm^{-1}, i.e., shifted toward lower wavenumber in comparison with its position in phosphorus oxychloride (1,365 cm^{-1}). This shifting may be due to replacement of the more electronegative chlorine atom by the dithiocarbonate moiety. The absorption bands at 442–425 (**3a**–**3h**) and 625–612 cm^{-1} (**4a**–**4h**) are assigned to ν (P–Cl) and (P(O)–Cl) vibrations, respectively, which show a negative shift compared with ν (P–Cl) and (P(O)–Cl) vibrations of PCl_3 (585–550 cm^{-1}) and $POCl_3$ (645–630 cm^{-1}). However, the disappearance of these absorption bands in the IR spectra of compounds **3i**–**3l** and **4i**–**4l** indicates the complete removal of the chloride ion, which led to the formation of the P–S–C chemical linkage in these derivatives.

^{31}P NMR

In the ^{31}P NMR spectra of compounds **3a**–**3d**, the signal for the phosphorus atom was found at $\delta = 192.6$–193.6 ppm, i.e., 23–30 ppm upfield from its position in free phosphorus trichloride (221 ppm). The phosphorus signal of compounds **3e**–**3l** was observed at 166.3–184.5 ppm, i.e., 14–26 ppm upfield compared with the corresponding signals for derivatives **3a**–**3d**. The further lowering in the chemical shifts may be attributed to the replacement of the more electronegative chloride moieties by the dithio moieties. The phosphorus signal for compounds **4a**–**4l** was observed at 6.5–19.5 ppm, i.e., downfield compared with its position in free $POCl_3$ (-1.9 ppm). The shielding in these compounds compared with compounds **3a**–**3l** may be correlated to the presence of the more electronegative oxygen atom. The appearance of only one phosphorus signal may be considered as an authentication of the purity of the compounds.

^{1}H NMR

In the ^{1}H NMR spectra, the signals for the $-CH_3$ (tolyl ring) and $-CH_2$ (benzyl ring) protons were observed at $\delta = 2.2$–2.4 and 4.5–4.6 ppm as singlets. The protons of the C_6H_4 (tolyl ring) and C_6H_5 (benzyl ring) gave signals in the range 6.6–7.1 and 7.1–7.2 ppm as multiplets. Compounds **3a**–**3l** and **4a**–**4l** did not show any appreciable deviation compared to the sodium salts of the dithiocarbonate ligands **1a**–**1d**.

^{13}C NMR

The ^{13}C NMR spectra of these ligands and their derivatives showed signals for all carbon nuclei in their characteristic regions. The signals for methyl ($-CH_3$) and methylene ($-CH_2$) carbon occurred in the range $\delta = 19.6$–21.4 and 70.8–71.4 ppm, respectively. The carbon nuclei of phenyl groups ($-C_6H_5$ and $-C_6H_4$) displayed their resonance in the region 112.0–135.3 ppm. The carbon attached to the methyl and methylene group in the respective compounds appeared at 122.9–135.2 and 136.8–137.4 ppm, respectively. The signal in the region 147.3–152.9 ppm was due to the carbon attached to the oxygen in the tolyl derivatives. The signal for the dithiocarbonate carbon ($-(O)CS_2$) appeared at 163.6–175.8 ppm in compounds **3a**–**3l** and **4a**–**4l**, whereas these signals were observed at 195.1–200.7 ppm in the parent ligands **1a**–**1d**. Presumably, this reflects the fact that the environment around the CS_2 carbon is the one most affected by the formation of the P–S covalent bond, thereby supporting the authenticity of these compounds.

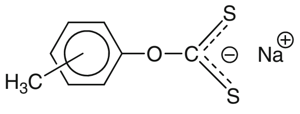
Mass spectra

The mass spectra of the dithiocarbonate ligands showed a molecular ion peak [M^+] at $m/z = 206.1$, suggesting the compounds were monomeric in nature. Some other peaks corresponding to [CS_2] 76.0, [HCS_2OH] 94.0, and [$C_8H_7OS_2]_2$ 366.0 were also observed. The mass spectra of a few representative phosphorus(III) and (V) compounds **3a**, **3f**, **3k**, **3l**, **4b**, **4e**, **4g** and **4l** had their molecular ion peak [M^+] at 285.5, 432.9, 580.8, 580.8, 301.1, 448.9, 448.9 and 596.8, respectively, which supported the assigned monomeric structure. Common peaks at 366.0, 108.0, and 76.0 were observed in the spectra of all the representative compounds due to the fragments [$C_8H_7OS_2]_2$, [C_7H_8OH], and [CS_2]. In addition to these molecular ion peaks, some other strong peaks were also observed, which were formed after the consecutive elimination of different groups. Moreover, compounds **3a** and **4b** that contain multiple chlorine atoms also show isotopic peaks of chlorine. The overlap of these isotope patterns was observed in the mass spectra. So, an isotopic envelope of three different peaks with distinctive ratios one to another spanning 2 mass units is observed around the molecular ion peak in the mass spectra of compounds **3a** and **4b**. The most intense isotopic peak in the mass spectra of compounds **3a** and **4b** at 285.0 and 301.0 was set at 100% and the percentage of other isotopic peaks was compared relative to it.

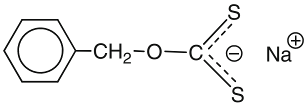
Structural features

On the basis of our IR, mass, and NMR (^{1}H, ^{13}C, and ^{31}P) spectral studies and in conjunction with the literature reports [37–49], a probable geometry may be assigned to these compounds. It is evident from the ^{13}C NMR spectra of all compounds that the peak in the region $\delta = 165.0$–201.7 ppm is characteristic of the CS_2 group which further supports the authenticity of these compounds. Therefore, in conjunction with the literature reports [37–49], the following type of general structure may be deduced for the sodium salt of (*o*-, *m*-, and *p*-cresyl/benzyl) dithiocarbonate ligands akin to that of ditolyldithiophosphate [51]. The ^{31}P chemical shift values favor the formation of these compounds with a monodentate linkage between the dithiocarbonate ligand and the phosphorus atom. Thus, a probable geometry around the phosphorus(III) (**3a**–**3l**) and phosphorus(V) (**4a**–**4l**) in different coordination spheres may tentatively be assigned to these compounds as shown in Fig. 1.

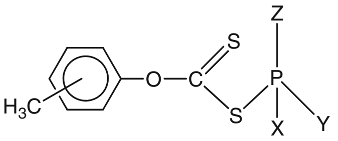
Fig. 1 Proposed structures of the prepared dithiocarbonates



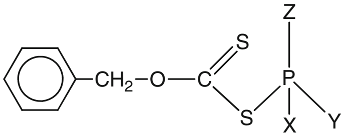
1a-1c



1d



X and Y = Cl for **3a-3c** and **4a-4c**; X = (*o*-, *m*-, *p*-$CH_3C_6H_4OCS_2$-) and Y = Cl for **3e-3g** and **4e-4g**; X and Y = (*o*-, *m*-, *p*-$CH_3C_6H_4OCS_2$-) for **3i-3k** and **4i-4k**; Z = lone pair of electrons for **3a-3c**, **3e-3g**, and **3i-3k** and doubly bonded oxygen for **4a-4c**, **4e-4g**, and **4i-4k**



X and Y = Cl for **3d** and **4d**; X = ($C_6H_5CH_2OCS_2$-) and Y = Cl for **3h** and **4h**; X and Y = ($C_6H_5CH_2OCS_2$-) for **3l** and **4l**; Z = lone pair of electrons for **3d**, **3h**, and **3l** and doubly bonded oxygen for **4d**, **4h**, and **4l**

Experimental

Toluene (Thomas Baker, b.p. 110 °C) and *n*-hexane (Thomas Baker, b.p. 68–69 °C) were freshly dried over sodium wire. Cresols (*o*-, *m*-, and *p*-) and benzyl alcohol (Thomas Baker, b.p. 191, 203, 202, and 205 °C) were also purified by distillation prior to use. The mass spectra were recorded on a Bruker esquire3000_00037 spectrophotometer. IR spectra were recorded either as KBr pellets or Nujol mulls in the range of 4,000–400 cm^{-1} on a Shimadzu 8201 PC and Perkin Elmer 557 spectrophotometer. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ on a Bruker Avance II 400 spectrometer using TMS as internal reference for ^1H and ^{13}C or H_3PO_4 (85%) as external reference for ^{31}P. The elemental analyses (C, H, Cl, and S) of these compounds were found to be consistent with their molecular formula. Sulfur was analyzed gravimetrically as $BaSO_4$ by Messenger's method and chlorine was estimated volumetrically by Volhard's method. Elemental analyses of C and H were carried out on a CHNS-932 Leco elemental analyzer. Moisture was carefully excluded throughout the experimental manipulations by using standard Schlenk techniques.

Sodium O-(2-methylphenyl)carbonodithioate
(**1a**, $C_8H_7NaOS_2$)

To a toluene solution (ca. 40 cm^3) of 2.00 g freshly distilled *o*-cresol (18.50 mmol) was added 0.43 g sodium metal (18.50 mmol). The contents were refluxed for 3 h until white precipitates started appearing and the refluxing was continued until sodium metal was completely dissolved. The contents were cooled using an ice bath at 0–5 °C. Subsequently, CS_2 was added to the reaction mixture dropwise over a period of 30 min with constant stirring. The contents were further stirred for 3 h during which the color changed from white to yellow. Compound **1a** was isolated by filtration using a funnel fitted with a G-4 sintered disc. The salt so obtained was washed with *n*-hexane and finally dried under reduced pressure that resulted in the formation of *o*-$CH_3C_6H_4OCS_2Na$ (**1a**) as pale yellow solid. Yield: 65%; m.p.: 197 °C (dec); IR (KBr): $\bar{\nu} = 3{,}022, 1{,}590, 1{,}142, 1{,}042, 1{,}004\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 2.3$ (s, 3H, CH_3), 6.6 (d, 1H, *ortho*), 6.7 (m, 2H, *meta*), 6.9 (t, 1H, *para*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 22.9$ (CH_3), 114.3 (C-*ortho*), 120.0 (C-*para*), 123.3 (C–CH_3), 126.1–128.8 (C-*meta*), 167.0 (C–O), 195.1 (OCS_2) ppm; EI-MS: *m*/*z* (%) = 366.2 (90)

$[(o\text{-}CH_3C_6H_4OCS_2)_2]^-$, 336.2 (22) $[(C_6H_5CS_2)_2]^-$, 206.1 (100) $[o\text{-}CH_3C_6H_4OCS_2Na]^+$, 183.0 (44) $[o\text{-}CH_3C_6H_4OCS_2]^-$, 168.0 (44) $[o\text{-}C_6H_5OCS_2]^-$, 130.0 (22) $[o\text{-}CH_3C_6H_4ONa]^-$, 108.0 (22) $[o\text{-}CH_3C_6H_4OH]^+$, 91.0 (11) $[o\text{-}CH_3C_6H_4]^+$, 76.0 (9) $[CS_2]^+$.

Sodium O-(3-methylphenyl)carbonodithioate (**1b**, $C_8H_7NaOS_2$)

Compound **1b** was synthesized according to the procedure described for **1a**; 2.00 g of $m\text{-}CH_3C_6H_4OH$ (18.50 mmol) and 0.43 g of Na (18.50 mmol) were used to give **1b** as a yellow solid. Yield: 67%; m.p.: 196 °C (dec); IR (KBr): $\bar{\nu}$ = 3,023, 1,596, 1,140, 1,040, 1,002 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.3 (s, 3H, CH_3), 6.6 (m, 2H, *ortho*), 6.8 (d, 1H, *para*), 7.0 (t, 1H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 22.7 (CH_3), 112.7–116.4 (C-*ortho*), 127.0 (C-*para*), 129.7 (C-*meta*), 135.0 (C–CH_3), 167.0 (C–O), 197.5 (OCS_2) ppm.

Sodium O-(4-methylphenyl)carbonodithioate (**1c**, $C_8H_7NaOS_2$)

Compound **1c** was synthesized according to the procedure described for **1a**; 2.00 g of $p\text{-}CH_3C_6H_4OH$ (18.50 mmol) and 0.43 g of Na (18.50 mmol) were used to give **1c** as a yellow solid. Yield: 65%; m.p.: 196 °C (dec); IR (KBr): $\bar{\nu}$ = 3,022, 1,593, 1,142, 1,040, 1,007 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.3 (s, 3H, CH_3), 6.8 (d, 2H, *ortho*), 6.9 (d, 2H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 22.0 (CH_3), 117.0 (C-*ortho*), 128.7 (C–CH_3), 129.6 (C-*meta*), 166.0 (C–O), 195.6 (OCS_2) ppm.

Sodium O-benzylcarbonodithioate (**1d**, $C_8H_7NaOS_2$)

Compound **1d** was synthesized according to the procedure described for **1a**; 2.00 g of $C_6H_5CH_2OH$ (18.50 mmol) and 0.43 g of Na (18.50 mmol) were used to give **1d** as a yellow solid. Yield: 75%; m.p.: 186 °C (dec); IR (KBr): $\bar{\nu}$ = 2,991, 1,610, 1,145, 1,045, 1,008 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 4.5 (s, 2H, CH_2), 7.1–7.2 (m, 5H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): δ = 75.2 (CH_2), 121.0–123.1 (C-*ortho*), 125.0–126.2 (C-*meta*), 126.4 (C-*para*), 140.2 (C–CH_2), 200.7 (OCS_2) ppm.

(2-Methylphenyl)oxycarbonothioylthiophosphorus(III) dichloride (**3a**, $C_8H_7Cl_2OPS_2$)

To a suspension of 1.00 g **1a** (4.85 mmol) in toluene (ca. 35 cm^3) was added a toluene solution (ca. 15 cm^3) of 0.67 g phosphorus trichloride (4.85 mmol). The reaction mixture was vigorously stirred for about 3 h. Subsequently, the contents were refluxed for 6 h during which a white precipitate of NaCl was formed. The reaction mixture was allowed to reach room temperature then filtered through a funnel fitted with a G-4 sintered disc. The excess solvent was then removed under reduced pressure followed by drying in vacuo for 3 h, which yielded $o\text{-}CH_3C_6H_4OCS_2PCl_2$ (**3a**) as pale yellow viscous liquid. Yield: 86%; IR (Nujol): $\bar{\nu}$ = 3,320, 1,583, 1,163, 1,017, 926, 556, 442 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.2 (s, 3H, CH_3), 6.7 (m, 2H, *meta*), 6.8 (d, 1H, *ortho*), 7.0 (t, 1H, *para*) ppm; ^{13}C NMR ($CDCl_3$): δ = 19.7 (CH_3), 114.3 (C-*ortho*), 119.1 (C-*para*), 122.9 (C–CH_3), 130.0–130.2 (C-*meta*), 152.5 (C–O), 165.2 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): δ = 192.6 ppm; EI-MS: *m*/*z* (%) = 366.5 (95) $[(o\text{-}CH_3C_6H_4OCS_2)_2]^+$, 285.5, 287.5, 289.5 (100, 50, 4) $[o\text{-}CH_3C_6H_4OCS_2PCl_2]^-$, 249.7 (9) $[o\text{-}CH_3C_6H_4OCS_2PCl]^-$, 214.2 (13) $[o\text{-}CH_3C_6H_4OCS_2P]^-$, 195.0, 197.0, 199.0 (47, 24, 2) $[CS_2OHPCl_2]^-$, 108 (26) $[o\text{-}CH_3C_6H_4OH]^-$, 96.0 (7) $[PS_2H]^+$, 76.0 (7) $[CS_2]^-$.

(3-Methylphenyl)oxycarbonothioylthiophosphorus(III) dichloride (**3b**, $C_8H_7Cl_2OPS_2$)

The synthesis of **3b** was carried out as described for **3a**; 1.00 g of **1b** (4.85 mmol) and 0.67 g of PCl_3 (4.85 mmol) were used to give **3b** as a pale yellow viscous liquid. Yield: 84%; IR (Nujol): $\bar{\nu}$ = 3,362, 1,584, 1,162, 1,018, 927, 535, 430 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.2 (s, 3H, CH_3), 6.8 (m, 2H, *ortho*), 6.9 (d, 1H, *para*), 7.0 (t, 1H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 20.3 (CH_3), 112.0–115.1 (C-*ortho*), 120.0 (C-*para*), 131.8 (C-*meta*), 134.3 (C–CH_3), 150.3 (C–O), 166.9 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): δ = 192.3 ppm.

(4-Methylphenyl)oxycarbonothioylthiophosphorus(III) dichloride (**3c**, $C_8H_7Cl_2OPS_2$)

The synthesis of **3c** was carried out as described for **3a**; 1.00 g of **1c** (4.85 mmol) and 0.67 g of PCl_3 (4.85 mmol) were used to give **3c** as a pale yellow viscous liquid. Yield: 87%; IR (Nujol): $\bar{\nu}$ = 3,401, 1,602, 1,165, 1,017, 920, 532, 428 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.2 (s, 3H, CH_3), 6.7 (d, 2H, *ortho*), 7.0 (d, 2H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 20.4 (CH_3), 115.4 (C-*ortho*), 130.1 (C–CH_3), 130.5 (C-*meta*), 152.9 (C–O), 167.4 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): δ = 193.0 ppm.

Benzyloxycarbonothioylthiophosphorus(III) dichloride (**3d**, $C_8H_7Cl_2OPS_2$)

The synthesis of **3d** was carried out as described for **3a**; 1.00 g of **1d** (4.85 mmol) and 0.67 g of PCl_3 (4.85 mmol) were used to give **3d** as a pale yellow viscous liquid. Yield: 90%; IR (Nujol): $\bar{\nu}$ = 3,384, 1,583, 1,162, 1,043, 926, 523, 430 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 4.5 (s, 2H, CH_2), 7.1–7.2 (m, 5H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): δ = 71.2 (CH_2), 126.1–126.2 (C-*ortho*), 127.5–127.6 (C-*meta*), 128.0 (C-*para*), 137.4 (C–CH_2), 166.9 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): δ = 193.6 ppm.

Bis[(2-methylphenyl)oxycarbonothioylthio]phosphorus(III) chloride (**3e**, $C_{16}H_{14}ClO_2PS_4$)

Compound **3e** was prepared by a similar procedure as described for **3a**; 1.00 g of **1a** (4.85 mmol) and 0.33 g of PCl_3 (2.42 mmol) were used to give **3e** as a pale yellow viscous liquid. Yield: 85%; IR (Nujol): $\bar{\nu}$ = 3,359, 1,581, 1,165, 1,017, 923, 536, 429 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 2.2 (s, 6H, CH_3), 6.6 (d, 2H, *ortho*), 6.7 (m, 4H, *meta*), 7.1 (t, 2H, *para*) ppm; ^{13}C NMR ($CDCl_3$): δ = 19.8 (CH_3), 114.0 (C-*ortho*), 119.4 (C-*para*), 123.0 (C–CH_3), 129.1–129.5 (C-*meta*), 152.3 (C–O), 169.2 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): δ = 184.5 ppm.

Bis[(3-methylphenyl)oxycarbonothioylthio]phosphorus(III) chloride (**3f**, $C_{16}H_{14}ClO_2PS_4$)

Compound **3f** was prepared by a similar procedure as described for **3a**; 1.00 g of **1b** (4.85 mmol) and 0.33 g of PCl_3 (2.42 mmol) were used to give **3f** as a pale yellow viscous liquid. Yield: 87%; IR (Nujol): $\bar{\nu}$ = 3,420, 1,583, 1,163, 1,023, 930, 550, 440 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 2.2 (s, 6H, CH_3), 6.8 (m, 4H, *ortho*), 6.9 (d, 2H, *para*), 7.0 (t, 2H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 20.8 (CH_3), 111.9–114.7 (C-*ortho*), 121.2 (C-*para*), 132.0 (C-*meta*), 134.2 (C–CH_3), 150.9 (C–O), 164.4 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): δ = 180.3 ppm; EI-MS: *m*/*z* (%) = 432.9 (51) $[(m\text{-}CH_3C_6H_4OCS_2)_2PCl]^+$, 366.5 (100) $[(m\text{-}CH_3C_6H_4OCS_2)_2]^+$, 282.7 (64) $[m\text{-}CH_3C_6H_4OCS_2PClSH]^-$, 259.4 (80) $[P(CS_2)_3]^+$, 252.7 (11) $[ClP(OHCS_2)_2]^+$, 170.2 (13) $[C_6H_5OCS_2H]^+$, 108.0 (18) $[m\text{-}CH_3C_6H_4OH]^+$, 76 (10) $[CS_2]^+$.

Bis[(4-methylphenyl)oxycarbonothioylthio]phosphorus(III) chloride (**3g**, $C_{16}H_{14}ClO_2PS_4$)

Compound **3g** was prepared by a similar procedure as described for **3a**; 1.00 g of **1c** (4.85 mmol) and 0.33 g of PCl_3 (2.42 mmol) were used to give **3g** as a pale yellow viscous liquid. Yield: 87%; IR (Nujol): $\bar{\nu}$ = 3,417, 1,602, 1,160, 1,018, 928, 537, 428 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 2.4 (s, 6H, CH_3), 6.9 (d, 4H, *ortho*), 7.1 (d, 4H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 19.6 (CH_3), 115.5 (C-*ortho*), 129.2 (C–CH_3), 129.3 (C-*meta*), 152.1 (C–O), 168.5 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): δ = 184.5 ppm.

Bis(benzyloxycarbonothioylthio)phosphorus(III) chloride (**3h**, $C_{16}H_{14}ClO_2PS_4$)

Compound **3h** was prepared by a similar procedure as described for **3a**; 1.00 g of **1d** (4.85 mmol) and 0.33 g of PCl_3 (2.42 mmol) were used to give **3h** as a pale yellow viscous liquid. Yield: 89%; IR (Nujol): $\bar{\nu}$ = 3,382, 1,584, 1,165, 1,015, 920, 526, 425 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 4.6 (s, 4H, CH_2), 7.1–7.2 (m, 10H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): δ = 71.0 (CH_2), 126.0–126.2 (C-*ortho*), 127.6–127.8 (C-*meta*), 128.2 (C-*para*), 137.3 (C–CH_2), 169.0 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): δ = 181.4 ppm.

Tris[(2-methylphenyl)oxycarbonothioylthio]phosphorus(III) (**3i**, $C_{24}H_{21}O_3PS_6$)

Compound **3i** was prepared by a similar procedure as described for **3a**; 1.00 g of **1a** (4.85 mmol) and 0.22 g of PCl_3 (1.60 mmol) were used to give **3i** as a pale yellow viscous liquid. Yield: 89%; IR (Nujol): $\bar{\nu}$ = 3,386, 1,601, 1,190, 1,040, 945, 530 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 2.2 (s, 9H, CH_3), 6.6 (d, 3H, *ortho*), 6.9 (m, 6H, *meta*), 7.1 (t, 3H, *para*) ppm; ^{13}C NMR ($CDCl_3$): δ = 19.7 (CH_3), 114.3 (C-*ortho*), 119.1 (C-*para*), 122.9 (C–CH_3), 129.1–129.5 (C-*meta*), 152.5 (C–O), 170.0 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): δ = 169.6 ppm.

Tris[(3-methylphenyl)oxycarbonothioylthio]phosphorus(III) (**3j**, $C_{24}H_{21}O_3PS_6$)

Compound **3j** was prepared by a similar procedure as described for **3a**; 1.00 g of **1b** (4.85 mmol) and 0.22 g of PCl_3 (1.60 mmol) were used to give **3j** as a pale yellow viscous liquid. Yield: 87%; IR (Nujol): $\bar{\nu}$ = 3,406, 1,607, 1,194, 1,017, 945, 538 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 2.2 (s, 9H, CH_3), 6.8 (m, 6H, *ortho*), 6.9 (d, 3H, *para*), 7.0 (t, 3H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 20.3 (CH_3), 112.1–114.8 (C-*ortho*), 121.0 (C-*para*), 131.8 (C-*meta*), 134.3 (C–CH_2), 150.3 (C–O), 171.5 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): δ = 169.6 ppm.

Tris[(4-methylphenyl)oxycarbonothioylthio]phosphorus(III) (**3k**, $C_{24}H_{21}O_3PS_6$)

Compound **3k** was prepared by a similar procedure as described for **3a**; 1.00 g of **1c** (4.85 mmol) and 0.22 g of PCl_3 (1.60 mmol) were used to give **3k** as a pale yellow viscous liquid. Yield: 89%; IR (Nujol): $\bar{\nu}$ = 3,385, 1,586, 1,180, 1,018, 940, 535 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 2.2 (s, 9H, CH_3), 6.7 (d, 6H, *ortho*), 7.1 (d, 6H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 20.4 (CH_3), 115.4 (C-*ortho*), 129.3 (C-*meta*), 130.1 (C–CH_3), 152.1 (C–O), 172.8 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): δ = 167.2 ppm; EI-MS: *m*/*z* (%) = 580.8 (56) $[p\text{-}(CH_3C_6H_4OCS_2)_3P]^+$, 490.6 (12) $[p\text{-}(CH_3C_6H_4OCS_2)_2PCS_2OH]^+$, 474.6 (15) $[p\text{-}(CH_3C_6H_4OCS_2)_2PCS_2H]^+$, 400.5 (16) $[p\text{-}CH_3C_6H_4OCS_2P(CS_2OH)_2]^+$, 397.5 (21) $[p\text{-}(CH_3C_6H_4OCS_2)_2P]^+$, 366.5 (10) $[p\text{-}(CH_3C_6H_4OCS_2)_2]^-$, 310.4 (100) $[(CS_2OH)_3P]^-$, 259.4 (26) $[P(CS_2)_3]^-$, 217.2 (5) $[(CS_2OH)_2P]^-$, 108.1 (34) $[p\text{-}CH_3C_6H_4OH]^+$, 96.1 (10) $[PS_2H]^+$, 76.1 (8) $[CS_2]^+$.

Tris(benzyloxycarbonothioylthio)phosphorus(III) (**3l**, $C_{24}H_{21}O_3PS_6$)

Compound **3l** was prepared by a similar procedure as described for **3a**; 1.00 g of **1d** (4.85 mmol) and 0.22 g of PCl_3 (1.60 mmol) were used to give **3l** as a pale yellow viscous liquid. Yield: 90%; IR (Nujol): $\bar{\nu}$ = 3,462, 1,581, 1,185, 1,015, 942, 525 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 4.5 (s, 6H, CH_2), 7.1–7.2 (m, 15H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): δ = 71.2 (CH_2), 126.1–126.2 (C-*ortho*), 127.6–127.8 (C-*meta*), 128.0 (C-*para*), 137.4 (C–CH_2), 175.8 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): δ = 167.2 ppm; EI-MS: *m*/*z* (%) = 580.8 (100) $[(C_6H_5CH_2OCS_2)_3P]^+$, 490.6 (9) $[(C_6H_5CH_2OCS_2)_2PCS_2OH]^+$, 400.5 (7) $[C_6H_5CH_2OCS_2P(CS_2OH)_2]^+$, 397.5 (7) $[(C_6H_5CH_2OCS_2)_2P]^-$, 366.5 (71)

$[(C_6H_5CH_2OCS_2)_2]^+$, 310.4 (51) $[P(CS_2OH)_3]^-$, 259.4 (24) $[P(CS_2)_3]^-$, 214.2 (27) $[C_6H_5CH_2OCS_2P]^+$, 108.1 (20) $[C_6H_5CH_2OH]^+$, 76.0 (10) $[CS_2]^+$.

[(2-Methylphenyl)oxycarbonothioylthio]oxophosphorus(V) dichloride (**4a**, $C_8H_7Cl_2O_2PS_2$)

The synthesis of **4a** was carried out as described for **3a** except the refluxing period, which was about 10 h; 1.00 g of **1a** (4.85 mmol) and 0.74 g of $POCl_3$ (4.85 mmol) were used to give **4a** as a pale yellow viscous liquid. Yield: 80%; IR (Nujol): $\bar{\nu} = 3{,}448, 1{,}584, 1{,}266, 1{,}165, 1{,}043, 927, 617, 525\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 2.2$ (s, 3H, CH_3), 6.8 (d, 1H, *ortho*), 6.9 (m, 2H, *meta*), 7.0 (t, 1H, *para*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.8$ (CH_3), 114.2 (C-*ortho*), 118.7 (C-*para*), 129.2 (C–CH_3), 129.8–130.3 (C-*meta*), 148.0 (C–O), 163.6 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 6.5$ ppm.

[(3-Methylphenyl)oxycarbonothioylthio]oxophosphorus(V) dichloride (**4b**, $C_8H_7Cl_2O_2PS_2$)

Compound **4b** was synthesized according to the procedure described for **4a**; 1.00 g of **1b** (4.85 mmol) and 0.74 g of $POCl_3$ (4.85 mmol) were used to give **4b** as a pale yellow viscous liquid. Yield: 80%; IR (Nujol): $\bar{\nu} = 3{,}383, 1{,}585, 1{,}267, 1{,}160, 1{,}040, 932, 612, 520\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 2.2$ (s, 3H, CH_3), 6.8 (m, 2H, *ortho*), 6.9 (d, 1H, *para*), 7.0 (t, 1H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 20.3$ (CH_3), 112.1–115.2 (C-*ortho*), 120.0 (C-*para*), 130.3 (C-*meta*), 135.2 (C–CH_3), 147.3 (C–O), 169.0 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 6.5$ ppm; EI-MS: *m/z* (%) = 366.5 (67) $[(m\text{-}CH_3C_6H_4OCS_2)_2]^+$, 301.1, 303.1, 305.1 (100, 50, 4) $[m\text{-}CH_3C_6H_4OCS_2POCl_2]^-$, 230.2 (15) $[m\text{-}CH_3C_6H_4OCS_2PO]^+$, 216.2 (8) $[C_6H_5OCS_2PO]^+$, 211.0, 213.0, 215.0 (16, 8, 1) $[POCl_2CS_2OH]^-$, 158.6 (13) $[CS_2POCl]^+$, 124.1 (10) $[POCS_2H]^-$, 108.1 (15) $[m\text{-}CH_3C_6H_4OH]^+$, 96.1 (7) $[PS_2H]^+$, 76.1 (14) $[CS_2]^+$.

[(4-Methylphenyl)oxycarbonothioylthio]oxophosphorus(V) dichloride (**4c**, $C_8H_7Cl_2O_2PS_2$)

Compound **4c** was synthesized according to the procedure described for **4a**; 1.00 g of **1c** (4.85 mmol) and 0.74 g of $POCl_3$ (4.85 mmol) were used to give **4c** as a pale yellow viscous liquid. Yield: 82%; IR (Nujol): $\bar{\nu} = 3{,}356, 1{,}584, 1{,}262, 1{,}175, 1{,}015, 940, 625, 529\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 2.2$ (s, 3H, CH_3), 6.8 (d, 2H, *ortho*), 7.1 (d, 2H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.2$ (CH_3), 120.2 (C-*ortho*), 130.5 (C–CH_3), 135.3 (C-*meta*), 148.6 (C–O), 163.6 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 6.5$ ppm.

(Benzyloxycarbonothioylthio)oxophosphorus(V) dichloride (**4d**, $C_8H_7Cl_2O_2PS_2$)

Compound **4d** was synthesized according to the procedure described for **4a**; 1.00 g of **1d** (4.85 mmol) and 0.74 g of $POCl_3$ (4.85 mmol) were used to give **4d** as a pale yellow viscous liquid. Yield: 85%; IR (Nujol): $\bar{\nu} = 3{,}412, 1{,}586, 1{,}265, 1{,}170, 1{,}017, 935, 620, 530\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 4.6$ (s, 2H, CH_2), 7.1–7.2 (m, 5H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 70.8$ (CH_2), 126.0–126.1 (C-*ortho*), 127.5–127.6 (C-*meta*), 128.1 (C-*para*), 137.4 (C–CH_2), 165.4 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 7.5$ ppm.

Bis[(2-methylphenyl)oxycarbonothioylthio]oxophosphorus(V) chloride (**4e**, $C_{16}H_{14}ClO_3PS_4$)

Compound **4e** was synthesized according to the procedure described for **4a** except the refluxing period, which was about 11 h; 1.00 g of **1a** (4.85 mmol) and 0.37 g of $POCl_3$ (2.42 mmol) were used to give **4e** as a pale yellow viscous liquid. Yield: 81%; IR (Nujol): $\bar{\nu} = 3{,}386, 1{,}584, 1{,}270, 1{,}164, 1{,}018, 926, 621, 524\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 2.2$ (s, 6H, CH_3), 6.9 (d, 2H, *ortho*), 7.0 (m, 4H, *meta*), 7.1 (t, 2H, *para*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 20.8$ (CH_3), 115.2 (C-*ortho*), 119.4 (C-*para*), 129.0 (C–CH_3), 129.8–130.3 (C-*meta*), 148.3 (C–O), 169.0 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 15.2$ ppm; EI-MS: *m/z* (%) = 448.9 (100) $[(o\text{-}CH_3C_6H_4OCS_2)_2POCl]^+$, 413.5 (7) $[(o\text{-}CH_3C_6H_4OCS_2)_2PO]^+$, 358.9 (34) $[(o\text{-}CH_3C_6H_4OCS_2)POCl(CS_2OH)]^+$, 323.4 (21) $[(o\text{-}CH_3C_6H_4OCS_2)PO(CS_2OH)]^+$, 268.7 (57) $[(CS_2OH)_2POCl]^+$, 234.7 (51) $[(CS_2)_2POCl]^-$, 199.2 (34) $[(CS_2)_2PO]^+$, 108.1 (76) $[o\text{-}CH_3C_6H_4OH]^+$, 96.1 (14) $[PS_2H]^+$, 76.1 (8) $[CS_2]^+$.

Bis[(3-methylphenyl)oxycarbonothioylthio]oxophosphorus(V) chloride (**4f**, $C_{16}H_{14}ClO_3PS_4$)

Compound **4f** was synthesized according to the procedure described for **4e**; 1.00 g of **1b** (4.85 mmol) and 0.37 g of $POCl_3$ (2.42 mmol) were used to give **4f** as a pale yellow viscous liquid. Yield: 80%; IR (Nujol): $\bar{\nu} = 3{,}385, 1{,}584, 1{,}276, 1{,}165, 1{,}043, 930, 617, 525\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 2.2$ (s, 6H, CH_3), 6.8 (m, 4H, *ortho*), 6.9 (t, 2H, *meta*), 7.0 (d, 2H, *para*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 20.8$ (CH_3), 112.1–115.2 (C-*ortho*), 119.9 (C-*para*), 130.3 (C-*meta*), 135.2 (C–CH_3), 148.4 (C–O), 164.9 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 15.0$ ppm.

Bis[(4-methylphenyl)oxycarbonothioylthio]oxophosphorus(V) chloride (**4g**, $C_{16}H_{14}ClO_3PS_4$)

Compound **4 g** was synthesized according to the procedure described for **4e**; 1.00 g of **1c** (4.85 mmol) and 0.37 g of $POCl_3$ (2.42 mmol) were used to give **4g** as a pale yellow viscous liquid. Yield: 83%; IR (Nujol): $\bar{\nu} = 3{,}418, 1{,}585, 1{,}280, 1{,}172, 1{,}032, 943, 615, 560\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 2.2$ (s, 6H, CH_3), 6.9 (d, 4H, *ortho*), 7.0 (d, 4H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.4$ (CH_3), 120.2 (C-*ortho*), 131.2 (C–CH_3), 134.8 (C-*meta*), 148.6 (C–O), 172.3 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 15.2$ ppm; EI-MS: *m/z* (%) = 448.9 (100) $[(p\text{-}CH_3C_6H_4OCS_2)_2POCl]^+$, 366.1 (20) $[(p\text{-}CH_3C_6H_4OCS_2)_2]^+$, 268.7 (36) $[(CS_2OH)_2POCl]^-$, 234.9 (11) $[(CS_2)_2POCl]^+$, 199.9 (11) $[(CS_2)_2PO]^+$, 108.1 (22) $[p\text{-}CH_3C_6H_4OH]^+$, 76.1 (28) $[CS_2]^+$.

Bis(benzyloxycarbonothioylthio)oxophosphorus(V) chloride (**4h**, $C_{16}H_{14}ClO_3PS_4$)

Compound **4h** was synthesized according to the procedure described for **4e**; 1.00 g of **1d** (4.85 mmol) and 0.37 g of $POCl_3$ (2.42 mmol) were used to give **4h** as a pale yellow viscous liquid. Yield: 85%; IR (Nujol): $\bar{\nu} = 3{,}402, 1{,}585, 1{,}285, 1{,}180, 1{,}024, 944, 612, 564\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 4.5$ (s, 4H, CH_2), 7.2 (m, 10H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 71.2$ (CH_2), 125.7–125.8 (C-*ortho*), 126.9–127.1 (C-*meta*), 127.9 (C-*para*), 137.0 (C–CH_2), 167.8 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 14.9$ ppm.

Tris[(2-methylphenyl)oxycarbonothioylthio]oxophosphorus(V) (**4i**, $C_{24}H_{21}O_4PS_6$)

Compound **4i** was synthesized according to the procedure described for **4a** except the refluxing period, which was about 12 h; 1.00 g of **1a** (4.85 mmol) and 0.25 g of $POCl_3$ (1.62 mmol) were used to give **4i** as a pale yellow viscous liquid. Yield: 82%; IR (Nujol): $\bar{\nu} = 3{,}432, 1{,}603, 1{,}290, 1{,}185, 1{,}018, 942, 537\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 2.2$ (s, 9H, CH_3), 6.8 (d, 3H, *ortho*), 6.9 (m, 6H, *meta*), 7.0 (t, 3H, *para*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.7$ (CH_3), 114.1 (C-*ortho*), 118.7 (C-*para*), 128.2-129.2 (C-*meta*), 129.0 (C–CH_3), 147.3 (C–O), 168.6 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 19.4$ ppm.

Tris[(3-methylphenyl)oxycarbonothioylthio]oxophosphorus(V) (**4j**, $C_{24}H_{21}O_4PS_6$)

Compound **4j** was synthesized according to the procedure described for **4i**; 1.00 g of **1b** (4.85 mmol) and 0.25 g of $POCl_3$ (1.62 mmol) were used to give **4j** as a pale yellow viscous liquid. Yield: 80%; IR (Nujol): $\bar{\nu} = 3{,}429, 1{,}602, 1{,}282, 1{,}183, 1{,}025, 943, 538\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 2.2$ (s, 9H, CH_3), 6.6 (m, 6H, *ortho*), 7.0 (d, 3H, *para*), 7.1 (t, 3H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 20.3$ (CH_3), 112.2–114.7 (C-*ortho*), 120.0 (C-*para*), 131.2 (C-*meta*), 134.2 (C–CH_3), 148.3 (C–O), 169.2 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 19.5$ ppm.

Tris[(4-methylphenyl)oxycarbonothioylthio]oxophosphorus(V) (**4k**, $C_{24}H_{21}O_4PS_6$)

Compound **4k** was synthesized according to the procedure described for **4i**; 1.00 g of **1c** (4.85 mmol) and 0.25 g of $POCl_3$ (1.62 mmol) were used to give **4k** as a pale yellow viscous liquid. Yield: 81%; IR (Nujol): $\bar{\nu} = 3{,}379, 1{,}603, 1{,}285, 1{,}180, 1{,}018, 944, 555\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 2.2$ (s, 9H, CH_3), 6.8 (d, 6H, *ortho*), 7.1 (d, 6H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.2$ (CH_3), 121.1 (C-*ortho*), 131.0 (C–CH_3), 135.3 (C-*meta*), 148.9 (C–O), 170.0 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 19.4$ ppm.

Tris(benzyloxycarbonothioylthio)oxophosphorus(V)
(**4l**, $C_{24}H_{21}O_4PS_6$)

Compound **4l** was synthesized according to the procedure described for **4i**; 1.00 g of **1d** (4.85 mmol) and 0.25 g of $POCl_3$ (1.62 mmol) were used to give **4l** as a pale yellow viscous liquid. Yield: 86%; IR (Nujol): $\bar{\nu} = 3{,}362, 1{,}585, 1{,}277, 1{,}185, 1{,}024, 942, 540\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 4.6$ (s, 6H, CH_2), 7.1–7.2 (m, 15H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 71.4$ (CH_2), 125.7–125.9 (C-*ortho*), 126.7–126.8 (C-*meta*), 128.0 (C-*para*), 136.8 (C–CH_2), 171.5 (OCS_2) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 19.5$ ppm; EI-MS: *m/z* (%) = 596.8 (72) $[(C_6H_5CH_2OCS_2)_3PO]^+$, 446.6 (8) $[(C_6H_5CH_2OCS_2)_2POSH]^+$, 417.5 (19) $[(C_6H_5CH_2OCS_2)_2POH]^-$, 275.8 (100) $[(CS_2)_3PO]^-$, 263.0 (12) $[C_6H_5CH_2OCS_2POSH]^-$, 230.2 (20) $[C_6H_5CH_2OCS_2PO]^+$, 199.8 (25) $[(CS_2)_2PO]^+$, 146.2 (15) $[(SH)_3PO]^+$, 108.1 (38) $[C_6H_5CH_2OH]^+$, 76.1 (19) $[CS_2]^+$.

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