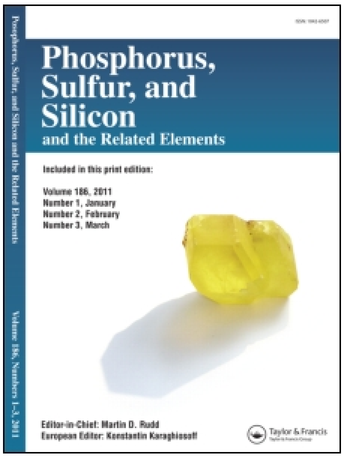


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Synthesis and Evalution of Novel Aryl-Substituted Dithioimidophosphonates as an Extrantant for Metals

Ruiren Tang[ab]; Cancheng Gou[ab]
[a] School of Chemistry and Chemical Engineering, Hunan University, Changsha, People's Republic of China [b] School of Chemistry and Chemical Engineering, Central South University, Changsha, People's Republic of China

To cite this Article Tang, Ruiren and Gou, Cancheng(2005) 'The Synthesis and Evalution of Novel Aryl-Substituted Dithioimidophosphonates as an Extrantant for Metals', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 12, 2725 — 2731

To link to this Article: DOI: 10.1080/104265090968064

URL: http://dx.doi.org/10.1080/104265090968064

Phosphorus, Sulfur, and Silicon, 180:2725–2731, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090968064

Taylor & Francis
Taylor & Francis Group

The Synthesis and Evalution of Novel Aryl-Substituted Dithioimidophosphonates as an Extrantant for Metals

Ruiren Tang
School of Chemistry and Chemical Engineering, Hunan University, Changsha, People's Republic of China; School of Chemistry and Chemical Engineering, Central South University, Changsha, People's Republic of China

Cancheng Gou
School of Chemistry and Chemical Engineering, Hunan University, Changsha, People's Republic of China

A novel series of O,O′,O″,O‴-tetraaryldithioimidophonates $[(ArO)_2PS]_2NH$ **4** *were synthesized by the reaction of O,O,-diaryl phosphorochlorothionates* **2** *and diarylphosphonothioic amide under a strong basic condition. The key intermediates* ***2a∼2g*** *were prepared from thiophosphyl chloride and substituted phenols under phase transfer catalysis conditions for the first time. These teteraaryl dithioimidophonates show high selectivity for Zn^{2+} over Fe^{3+} from a sulfate solution. The effects of substituents on the ^{31}P NMR of the titled compounds also are discussed.*

Keywords ^{31}P-NMR; dithioimidophospoinates; extraction; synthesis

Dithiomimidophosphinate $(R_2XPNXPR_2)^-$($R{=}CH_3$, or C_6H_5; and X=S)[1] are important compounds with interesting structures which can form bis-coordinated complexes with divalent metals (such as Mn, Fe, Co, Ni, and Pt) with a MS_4 tetrahedral core[2–5] and can be used for metalloenzymes targets.[2–5] Recently, the Mrley, Eckhard, Bonford and their colleagues reported independently that tetra-alkyl substituted dithioimidophonates were powerful complexing agents for zinc from aqueous solution with good selectivity over iron.[6–8] Particularly the commercial success in the selective solvent extraction of copper from aqueous acidic solution derived from oxide ores using ring alkylated

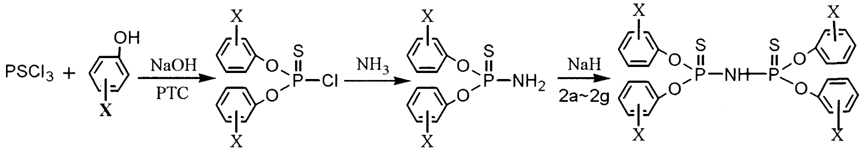
Received September 14, 2004; in final form March 1, 2005.

Financial support from the Natural Science Foundation of China (No. 20376018) is gratefully acknowledged.

Address correspondence to Cancheng Gou, Hunan University, School of Chemistry and Chemical Engineering, Changsha 410083, Peoples' Republic of China. E-mail: ccguo@mail.hunu.edu.cn

o-hydrobenzophenone oxime[6] and salicyladoxime has attracted great interest in related processes that could be used for the selective solvent extraction of other metals, especially for cases where the required metal is in smaller concentration in solution than main element. However, to our best knowledge, few articles about the aryl substituted dithioimidophonates and their applications in such an area have been reported in literature.

In order to explore the structures and the electronic properties of the ligands and their selectivity in complexing with metals, in this article, we report a facile method for preparing the key intermediates **2a**∼**2g** under phase-transfer catalyzed conditions and a series of novel aryl-substituted dithioimidophonates [(X-ArO)$_2$PS]NH (**4**). The synthetic route is shown in Scheme 1. All the products except for **2a** and **4a** have not been reported in literatures.



1 **2a~g** **3a~g** **4a~g**

Compound	a	b	c	d	e	f	g
X	H	*p*-CH_3	*o*-CH_3	*p*-OMe	*p*-NO_2	*p*-*t*-C_4H_9	*p*-Cl

Scheme 1

RESULTS AND DISCUSSION

We tried to prepare diaryl-phosphorochloridothionate (**2**) by the direct treatment of thiophosphyl chloride ($PSCl_3$) with a phenol, but surprisingly, $PSCl_3$ does not react with phenol even under forcing conditions. In the presence of aluminum chloride, phenol and $PSCl_3$ remained unchanged after 2 h at reflux. But, in the present of NaOH or triethylamine, as an acid acceptor $PSCl_3$ reacts with two equivalent phenol, and O,O-diarylphosphorochloridothionate (**2**) is prepared in moderate yield (see Table I, Non-Phase-Transfer Catalyst (PTC) conditions). Furthermore, the formation of byproducts such as mono-aryl derivatives [(ArO)P(S)Cl_2] and thiophosphates [(ArO)$_3$P(S)] is difficult to avoid. In an attempt to improve the yields of the reactions, Phase-Transfer-Catalysts[9] (PTCs) such as Tetra Butyl Ammonium Bromide (TBAB) and Benzyl Triethyl Ammonium Chloride (BTAC) have been used. As

TABLE I Preparation of $(X\text{-}ArO)_2$ PSCl Under PTCs

	Under PTC conditions/%		Non-PTC/%
Number	PTCs	Yield of 2	Yield of 2
2a	BTAC	71.0	57.6
2b	BTAC	79.3	43.8
2c	BTAC	74.6	49.3
2d	BTAC	77.1	52.1
2e	BTAC	80.0	50.7
2f	TABA	73.7	46.5
2g	BTAC	78.2	47.3

expected, the yields of **2a∼2f** were enhanced up to about 80%. Table I compared the yields of compound **2** with and without PTC.

The ^{1}H-NMR spectra of all compounds show that the two aryl groups in **2** or four aryl groups in **4** are magnetically identical and have resonance at the same frequency because of some relative position to the magnetically anisotropic benzene ring. On the other hand, the proton-decoupled ^{31}P-NMR spectra of compounds **4** in $CDCl_3$ show one signal at about $\delta = 50–55$, which was assigned to the major isomer **SS** in which the P atom is at the same chemical environments based on the ^{1}H NMR spectra, and not to the isomer **SH** in which proton-decoupled ^{31}P-NMR spectra should show two singlets for the two magnetically nonequivalent P nuclear (Scheme 2). Hence, the ^{31}P-NMR spectrometry provides a convenient means for distinguishing these isomers (**SS** and **SH**).

SS **SH**

Scheme 2

On the other hand, the ^{31}P-NMR chemical shifts δ of compound **4** correlate linearly with the Hammett $\sigma^{[10]}$ constants of the substituents X on the phenyl ring. The correlation between the ^{31}P-NMR chemical shifts of the P-atom of compound **4** and the Hammet constant (σ) of X[10] can be depicted by the following equation:

$$\delta_P = 1.6728\sigma + 50.5833$$

$$r = 0.96, n = 12, \text{ confidence level } 99.9. \quad (1)$$

A small-scale solvent extraction processes show the titled compounds are fairly strong extractants and have a high selectivity for zinc (Zn^{2+}) over iron (Fe^{3+}) from a sulfate solution. The extracting ability for zinc from a sulfate solutions is 4f > 4e > 4c > 4b > 4g > 4d > 4a. It needs further studies to illustrate the effects of electronic properties, steric effects of X, and other factors on their extracting and chelating behaviors.

EXPERIMENTAL

All reagents commercially available were purified and dried by the standard procedures. Analytical thin-layer TLC was performed on a 5 × 10 cm precoated silica gel F-254 with detection under ultraviolet light. Uncorrected melting points were determined on an XRC-1 apparatus. IR spectra were recorded on an Avatar 3600 spectrophotometer with KBr plates. ^{1}H-NMR and ^{31}P-NMR spectra were recorded with an INOVA-200 MHz apparatus in $CDCl_3$. MS were performed on an HP5988A spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer.

General Procedure for the Preparation of 2 Under PTC Conditions

To the suspension of 0.4 mol phenol and sodium hydroxide solution (16.0 g, 0.4 mol in 24 mL water) in 80 mL, benzene was added under vigorous stirring, then 1.2 mmol desired PTC was added to the reaction mixture, followed by the dropwise addition of $PSCl_3$ (34 g, 0.2 mol) from the additional funnel over a period of 30 min. The reaction was stirred until TLC showed no starting materials. Hundred milliliter of water was added and the organic phase was separated. The aqueous phase was extracted with 3 × 50 mL of benzene. The combined organic phase was washed with water until the pH = 7 was dried over anhydrous Na_2SO_4, was evaporated, and the crude product was purified by recrytalization give stable crystals.

2a

M.p.: 64–65°C. Yield 71.0%. ^{1}H NMR/δ: 7.14 (m, 10H, Ar′H). MS (m/e, %): 284 (M^+, 100), 286 (M+2, 33). IR (film) 1600, 1560, 1185, 750 cm^{-1}.

2b

M.p.: 71–73°C. Yield 79.3%. ^{1}H NMR/δ: 7.34~7.27 (d, 8H, J = 7.2 Hz, Ar′H), 2.31 (s, 6H, CH_3). MS (m/e, %): 312 (M^+, 90), 314 (M+2, 30), 91 (100). IR (film): 1590,1560, 1493, 1181, 748 cm^{-1}. Anal. cacld. for $C_{14}H_{14}O_2ClPS$: C 53.76, H 4.48; found: C 53.40; H 4.45.

2c

M.p.: 67–68°C. Yield 74.6%. ^1H NMR/δδ.28 (m, 8H, Ar′H), 2.24 (s, 6H, CH_3). MS (m/e, %): 312 (M^+, 90), 314 (M+2, 30), 91 (100). IR (film): 1601, 1578, 1477, 1180, 750 cm^{-1}.

2d

M.p.: 68–69°C. Yield 77.1%. ^1H NMR/δ: 7.23 (m, 8H, Ar′H), 3.59 (s, 6H, $0CH_3$). MS (m/e, %): 344 (M^+, 100), 346 (M+2, 33). IR (film): 1596, 1573, 1182, 741 cm^{-1}. Anal. cacld. for $C_{14}H_{14}O_4$ ClPS: C 48.76; H 4.06; found: C 48.48; H 3.97.

2e

M.p.: 75–76°C. Yield 80.0%. ^1H NMR/δ: 7.53 (d, 4H, J = 8.2 Hz, Ar′H), 8.42 (d, 4H, J = 7.9 Hz, Ar′H). MS (m/e, %): 374 (M^+, 100), 376 (M+2, 33). IR (film): 1587, 1523, 1458, 1356, 1187, 768 cm^{-1}. Anal. cacld. for $C_{12}H_8O_6$ ClPNS: C 38.45; H 2.14; N 7.48; found: C 38.79; H 2.08; N 7.39.

2f

M.p.: 81–83°C. Yield 73.7%. ^1H NMR/δ: 7.18 (m, 8H, Ar′H), 1.09 (s, 18H, t-C_4H_9). MS (m/e, %): 396 (M^+, 100), 398 (M+2, 33), 91 (100). IR (film): 1600, 1471, 1390, 1375, 1185, 750 cm^{-1}. Anal. cacld. for $C_{20}H_{26}O_4$ ClPS: C 60.53; H 6.56; found: C 60.72; H 6.54.

2g

M.p.: 91–93°C. Yield 78.2%. ^1H NMR/δ: 7.31 (dd, 4H, J_{AB} = 8.3 Hz, J_{PB} = 1.5 Hz), 7.35 (d, 4H, J_{AB} = 8.3 Hz). MS (m/e, %): 352 (M^+, 90), 354 (M+2, 90), 91 (100). IR (film): 3030, 1610, 1500, 790, 750 cm^{-1}. Anal. cacld. for $C_{12}H_8O_2Cl_3PS$: C 40.76; H 2.28; found: C 41.00; H 2.31.

General Procedure for the Preparation of 4

Ammoia gas was bubbled through a solution of O,O-diarylphosphorochloridothionate (0.1 mol) in 250 mL benzene while maintaining the reaction temperature below 40°C for 2 h. The reaction mixture was washed with water to remove ammonium chloride. The organic layer was separated, dried, and evaporated to give crude **3**, which was used directly for the next step.

Five gram of sodium hydride in parafine (80%) was slowly added to a wel-stirred solution of 0.1 mol of **3** and 100 mL anhydrous THF. After being refluxed for 2 h, the monosodium salt of **3** was formed. Then a solution of 0.1 mol of **2** in 100 mL anhydrous THF was added dropwise to the suspension reation mixture. The mixture was refluxed for about 6 h. Then the solvent was evaporated and the residue was diluted with 200 mL benzene, and washed with diluted hydrochloric acid (5%) and then water. The mixture was dried over Na_2SO_4 and evaporated. White or light color crystals were obtained after the recrystallization form ethanol and benzene.

4a

Yield: 54%, white powder, m.p. 109–111°C. IR: 3348, 1591, 1488, 890, 1017, 618 cm^{-1}. ^{1}HNMR: $\delta = 7.32$ (m, 20H, phenyl-H), 6.32 (s, 1H, NH); ^{31}PNMR, $\delta = 50.8$. MS (FAB): m/z = 513 (M^+, 90). Analysis (%): Calcd. for $C_{24}H_{21}NO_4P_2S_2$: C 56.14, H 4.09, N 2.73; found: C 56.36; H 3.97; N 3.04.

4b

Yield: 52%, white powder, m.p. 113–115°C. IR: 3348, 1591, 1488, 1017, 889, 748, 618 cm^{-1}.^{1}HNMR: $\delta = 7.18$ (d, 16H, J = 6.9 Hz, aryl-H); 5.72 (s, 1H, NH), 2.33 (s, 12H, CH_3); ^{31}PNMR, $\delta = 50.5$. MS (FAB): m/z = 569 (M^+, 91). Anal. cacld. for $C_{28}H_{29}NO_4P_2S_2$: C 59.05, H 5.10, N, 2.46; found: C 58.84, H 5.10, N, 2.27.

4c

Yield: 57%, white powder, m.p. 112–114°C. IR: 327, 1559, 1480, 1340, 1510, 1195, 630, 676 cm^{-1}. ^{1}HNMR: $\delta = 5.82$ (s, 1H, NH); 7.18 (m, 16H, aryl-H); 2.34 (s, 12H, CH_3); ^{31}PNMR, $\delta = 50.5$. MS (FAB): m/z 569 (M^+, 85). Anal. cacld. for $C_{28}H_{29}NO_4P_2S_2$: C 59.05; H 5.10; N 2.46; found: C 58.99; H 5.22; N 2.35.

4d

Yield: 55%, white powder, m.p. 98–101°C. IR: 3258, 1590, 1488, 880, 1017, 618, 748 cm^{-1}. ^{1}HNMR: $\delta = 5.82$ (d, 1H,b NH), 8.23–8.30 (dd, 16H, $J_{ab} = 6.9$ Hz, $J_{PB} = 1.3$ Hz, aryl-H), 4.13 (s, 12H, CH_3);^{31}PNMR, $\delta = 50.5$. MS (FAB): m/z = 633 (M^+, 95). Anal. cacld. for $C_{28}H_{29}NO_8P_2S_2$: C 53.08; H 4.49; N 2.21; found: C 52.94; H 4.38; N 2.29.

4e

Yield: 58%, light yellow powder, m.p. 218–220°C. IR: 3348, 1590, 1485, 889, 1017, 618, 748 cm^{-1}. ^{1}HNMR: $\delta = 6.00$ (s, 1H, NH), 7.78 (dd, 8H, $J_{AB} = 8.8$ Hz, $J_{PB} = 1.5$ Hz), 8.32 (d, 8H, $J_{AB} = 8.8$ Hz); ^{31}PNMR, $\delta = 50.5$. MS (FAB): m/z = 693 (M^+, 89); Anal. cacld. for

$C_{24}H_{17}N_5O_{12}P_2S_2$: C 41.56, H 2.46, N 10.10; found: C 41.21; H 2.41; N 10.32.

4f

Yield: 38%, white powder, m.p. 165–166°C. IR: 3235, 1605, 1509, 1495, 881, 1070, 630,749 cm^{-1}. ^{1}HNMR: $\delta = 5.60$ (s, 1H, NH), 7.23 (m, 16H, aryl-H), 1.12 (s, 36H,t-Bu-H). ^{31}PNMR, $\delta = 50.5$. MS (FAB): 737 (M^+,87). Anal. cacld. for $C_{40}H_{53}NO_4P_2S_2$: C 65.12; H 7.19; N 1.90; found: C 65.37; H 7.21; N 1.75.

4g

Yield: 56%, white powder, m.p. 126–128°C. IR: 3315, 1600, 1483, 900, 1010, 628, 740 cm^{-1}. ^{1}HNMR: $\delta = 5.88$ (d, 1H, NH), 7.25 (dd, 8H, $J_{\mathbf{AB}} = 8.2$ Hz, $J_{PB} = 1.5$ Hz), 7.36 (d, 8H, $J_{AB} = 8.2$ Hz). ^{31}PNMR, $\delta = 50.3$. MS (FAB): m/z = (%): 352 (M^+,81). Anal. cacld. for $C_{24}H_{12}Cl_4NO_4P_2S_2$: C 52.93; H 3.15; N 2.58; found: C 52.48; H 3.17; N 2.55.

REFERENCES

[1] O. Siiman and J. Vetuskey, *Inorg. Chem.*, **19,** 1672 (1980).

[2] J. P. Phillips, M. Z. Alexandra, J. P. Andrew, J. W. David, and J. D. Woollins, *J. Chem. Soc. Dalton Trans.*, 2467 (1995).

[3] A. M. Rossi, M. Marchi, and L. Marvelli, *J. Chem Soc. Dalton Trans.*, 723 (1993).

[4] M. Nouaman, Z. Zak, and E. Herrmann, *Inorganic. Ally. Chem.*, **619,** 1147–1153 (1993).

[5] R. J. White, P. S. Margolis, J. Trias, and Z. Yuan, *Current Opinion in Pharmacology*, **3,** 502 (2003).

[6] J. O. Mrley and M. H. Charlton, *J. Phys. Chem. A*, **102,** 6871 (1998).

[7] H. Eckhard, B. Oldrich, and S. Petr, *Phosph, Sulf., Silicon, and the Relat. Elem.*, **109–110**(1–4), 201–204 (1996).

[8] J. C. Banford and R. F. Dalton, USP 5433855. June 18, 1995.

[9] H. H. Fredman, *Pure and Appl. Chem.*, **58**, 857 (1986).

[10] C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.*, **91,** 169 (1991).