

*Dedicated to Professor Luminița Silaghi-Dumitrescu
on the occasion of her 65th anniversary*

DITHIOARSINATES REVISITED. A MINI-REVIEW

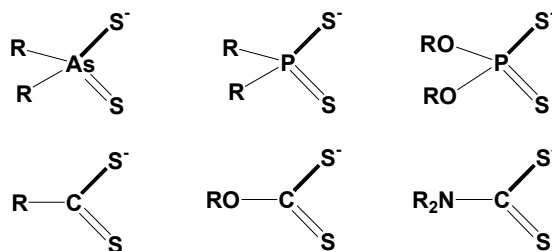
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ABSTRACT. The dithioarsinato ligands display a variety of coordination patterns in inorganic and organometallic compounds. Their structures and transformations are reviewed.

Keywords: dithioarsinate, 1,1-dithiolato ligands, self-assembly, organometallic, coordination.

1. INTRODUCTION

Dithioarsinates are members of a large family of anionic ligands, 1,1-dithiolates, which also includes dithiophosphinates, dithiophosphates, dithiocarboxylates, dithiocarbonates (xanthates) and dithiocarbamates (Scheme 1)[1]. Among these the dithioarsinates and dithiocarboxylates are less studied.



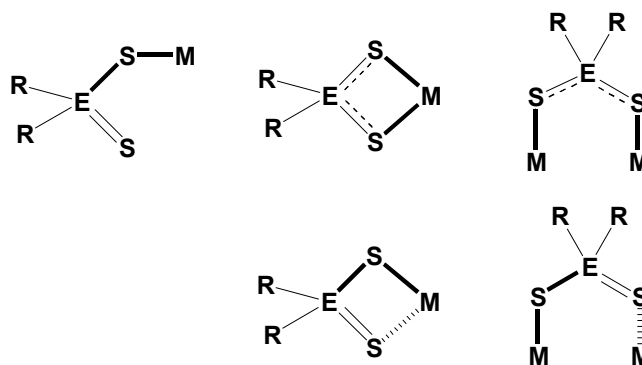
Scheme 1

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The 1,1-dithiolates are versatile ligands and display a variety of coordination patterns: monodentate, symmetric or unsymmetric bidentate chelating and bridging (Scheme 2, E = P or As). Our interest for this type of ligands was mainly stimulated by their ability to participate in the formation of inorganic (carbon-free) chelate rings [2].

The history of dithioarsinate chemistry has known three periods. After the preparation of the first metal dithioarsinates in the 19th century [3], the field lay dormant until the 70-thies of the 20th century, when the first X-ray structure determinations were performed. After a new period of some silence, the interest for the field was revitalized recently in particular due to the work of a group in Patras, Greece.



Scheme 2

2. TRANSITION METAL COMPLEXES

A series of dithioarsinates of chromium, manganese, cobalt, nickel, copper, zinc and indium was prepared from sodium dimethyldithioarsinate, $\text{Na}[\text{Me}_2\text{AsS}_2]$ and metal halides or by bubbling H_2S in a methanolic hydrochloric solution of the corresponding dimethylarsinates, $\text{M}[\text{Me}_2\text{AsO}_2]_n$, and the compounds were characterized by spectroscopic methods [4].

The transition metal dithioarsinates reported so far include dimethyldithioarsinates $\text{M}(\text{Me}_2\text{AsS}_2)_n$ with $\text{M} = \text{Cr}(\text{III})$, $n = 3$; $\text{M} = \text{Mn}(\text{II})$ [5a], $\text{Co}(\text{II})$ [5a, b], $\text{Cu}(\text{II})$ [5a,b,c] diphenyldithioarsinates $\text{M}(\text{S}_2\text{AsPh}_2)_n$, with $\text{M} = \text{Cr}(\text{III})$, and $\text{V}(\text{III})$, $n = 3$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $n = 2$; and $\text{M} = \text{In}(\text{III})$ [4c] and a dibenzylidithioarsinate $\text{Co}[\text{S}_2\text{As}(\text{CH}_2\text{Ph})_2]_2$ [6].

Oxovanadium $\text{VO}(\text{Me}_2\text{AsS}_2)_2$ and oxomolybdenum $\text{MoO}(\text{Me}_2\text{AsMe}_2)_3$ were also investigated in the same period [7].

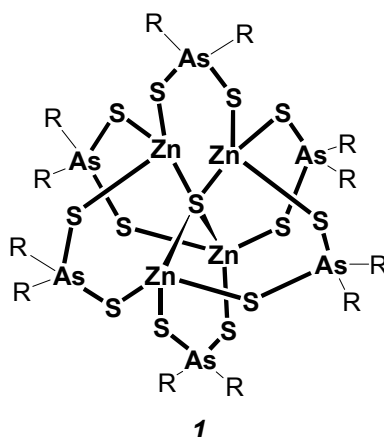
In a structural investigation the chromium complex $\text{Cr}(\text{Me}_2\text{AsS}_2)_3$ was found to display a distorted octahedral coordination geometry [8].

The complex $(\text{Me}_2\text{AsS}_2)_2\text{Pd}$ was prepared from sodium salt $\text{Na}[\text{Me}_2\text{AsS}_2] \cdot 2\text{H}_2\text{O}$, and $\text{Pd}(\text{OAc})_2$. The later also cleaves the disulfide $\text{Me}_2\text{As}(\text{S})\text{--S--AsMe}_2$ to form the complex $(\text{Me}_2\text{AsS}_2)_2\text{Pd}$, but this reacts further to form other $\text{Me}_2\text{As}(\text{S})$ compounds [9].

The copper(I) compound was obtained from $\text{Na}[\text{Me}_2\text{AsS}_2] \cdot 2\text{H}_2\text{O}$ with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and was also formed in the reaction of $\text{Me}_2\text{As}(\text{S})\text{--S--AsMe}_2$, with $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$, the compound $\text{Me}_2\text{As}(\text{S})\text{OAs}(\text{S})\text{Me}_2$ being also observed as by-product [10].

Of the post-transition metals of zinc and cadmium: form dimethyldithioarsinato complexes $\text{M}(\text{Me}_2\text{AsS}_2)_2$ [5a, b].

A spectacular compound is the tetrahedral oxo-centered inverse coordination complex $[(\mu_4\text{-S})\text{Zn}_4(\mu_2\text{-Me}_2\text{AsS}_2)_6]$ (**1**) in which the central sulfur atom is surrounded by four zinc atoms, bridged by six $[\text{Me}_2\text{AsS}_2]$ linkers. The structure was established by X-ray diffraction and a cadmium analogue was obtained [12]. The compound was prepared from $\text{Me}_2\text{As}(\text{S})\text{--S--AsMe}_2$ and $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in ethanol.



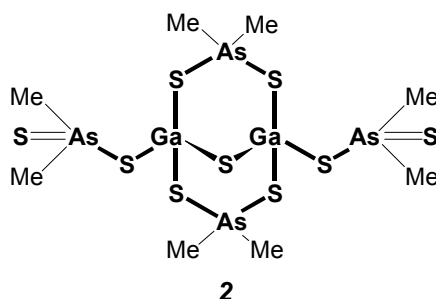
3. MAIN GROUP DERIVATIVES

The alkali metal dithioarsinates, $\text{M}[\text{R}_2\text{AsS}_2]$ ($\text{M} = \text{Na}$, $\text{R} = \text{Me}$ [11]; $\text{M} = \text{K}$, $\text{R} = \text{Ph}$, [4c], CH_2Ph [6]) are conveniently prepared from arsenic acids or their salts, $\text{M}[\text{R}_2\text{AsO}_2]$ by treatment with hydrogen sulfide. Two alkali metal dimethyldithioarsinates, namely the sodium salt $\text{Na}[\text{Me}_2\text{AsS}_2] \cdot 2\text{H}_2\text{O}$ [9] and the potassium salt $\text{K}[\text{Me}_2\text{AsS}_2] \cdot 2\text{H}_2\text{O}$, forming infinite bidimensional sheets, were structurally characterized by X-ray diffraction. [13].

Tris(dimethyldithioarsinato) complexes of Group 13 metals, $M(\text{Me}_2\text{AsS}_2)_3$ ($M = \text{Al, Ga, In, Tl}$) were recently prepared and characterized. [4c, 5b, 11, 14].

The indium(III) derivatives, $\text{In}(\text{S}_2\text{AsR}_2)_3$ ($R = \text{Me, Ph}$), studied by X-ray diffraction are monomeric distorted octahedral, and contain the dithioarsinates as isobidentate ligands [15]. The reaction of $\text{Na}[\text{Me}_2\text{AsS}_2] \cdot 2\text{H}_2\text{O}$ with $\text{Tl}(\text{OAc})_3$ gave $\text{Me}_2\text{AsS}_2\text{Tl}$ and $\text{Me}_2\text{As}(\text{S})\text{OAs}(\text{S})\text{Me}_2$ as by-product [10].

An interesting compound, $[(\text{Me}_2\text{AsS}_2)_2\text{Ga}]_2\text{S} \cdot 0.75\text{H}_2\text{O}$ (**2**), was formed in the hydrolysis (!) of $\text{Ga}(\text{Me}_2\text{AsS}_2)_3$. An X-ray diffraction analysis demonstrated its unique structure containing two monodentate and two bridging dithioarsinato ligands [16].



A number of dimethyl- and diphenyldithioarsinates of Main Group metals [$\text{Sn}(\text{IV})$, $\text{Pb}(\text{II})$, $\text{As}(\text{III})$, $\text{Sb}(\text{III})$, $\text{Bi}(\text{III})$] were synthesized [17]. The tris(dimethyldithioarsinato) complexes of group 15 metals, $M(\text{S}_2\text{AsMe}_2)_3$ ($M = \text{Sb, Bi}$) can be prepared by the reaction of $\text{Na}[\text{Me}_2\text{AsS}_2] \cdot 2\text{H}_2\text{O}$ with antimony trichloride and bismuth nitrate pentahydrate, respectively, but the reaction with AsCl_3 gave only $\text{Me}_2\text{As}(\text{S})\text{-S-AsMe}_2$ as isolable product [18].

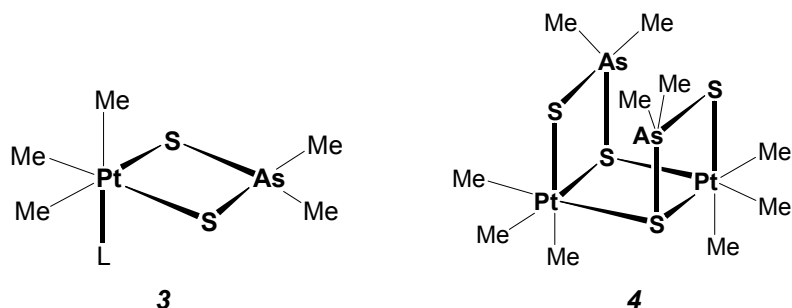
The crystal structure determination of bismuth dimethyldithioarsinate, $\text{Bi}(\text{S}_2\text{AsMe}_2)_3$ has found in the solid state that the compound is a dimeric supermolecule formed through $\text{Bi} \cdots \text{S}$ secondary bonds. [19]

4. ORGANOMETALLIC DERIVATIVES

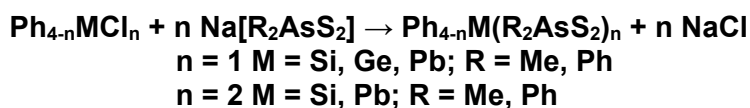
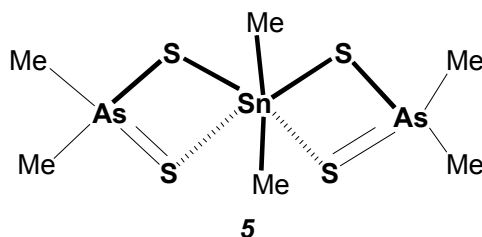
Very few organometallic dithioarsinato derivatives of transition metals have been reported; most known examples are dealing with main group metal compounds.

A rhenium(I) carbonyl complex $[\text{Re}(\text{CO})_3(\text{Me}_2\text{AsS}_2)\text{py}]$ has been described [20] and several trimethylplatinum compounds, including $[\text{PtMe}_3(\text{Me}_2\text{AsS}_2)\text{L}]$ (**3**), with $\text{L} = \text{py}$ or phosphines PMe_3 , PPh_3 , PMePh_2 , and a binuclear complex $[(\text{PtMe}_3)_2(\text{Me}_2\text{AsS}_2)_2]$ (**4**) have been reported with an X-ray diffraction study of the later [21].

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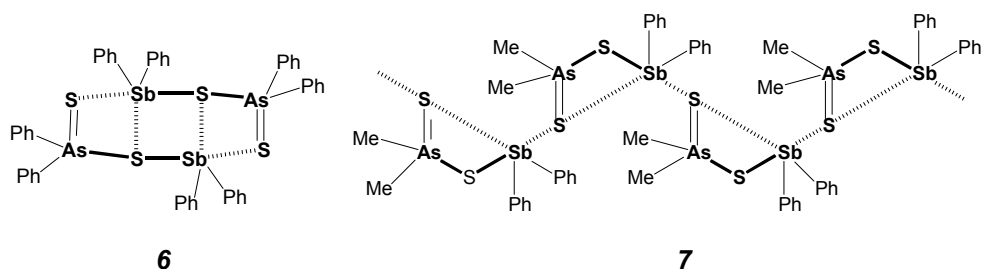
A series of organo-silicon, -germanium, -tin and -lead, derivatives of dimethyl- and diphenyldithioarsinic acids, $\text{Ph}_{4-n}\text{M}(\text{S}_2\text{AsR}_2)_n$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$; $n = 1$ and 2 , $\text{R} = \text{Me}, \text{Ph}$) were prepared. An X-ray structure analysis of $\text{Me}_2\text{Sn}(\text{S}_2\text{AsMe}_2)_2$ (**5**) established that the dithioarsinato ligand is anisobidentate [22]. On the basis of vibrational spectroscopy it was suggested that $\text{R}_3\text{Pb}(\text{S}_2\text{AsPh}_2)$ and $\text{R}_2\text{Pb}(\text{S}_2\text{AsPh}_2)$, contain Pb-As chelate rings, while in the analogous organosilicon and -germanium derivatives, the dithioarsinato ligand is monodentate.



Phenylantimony(III) dimethyldithioarsinates, $\text{Ph}_n\text{Sb}(\text{S}_2\text{AsMe}_2)_{3-n}$ with $n = 1-2$, have been prepared and the structure of $\text{Ph}_2\text{SbS}_2\text{AsMe}_2$ was determined by X-ray diffraction. The compound is a supramolecular compound, formed by self-assembly of molecular tectons into a chain-like structure with S-AsMe₂-S bridging ligands, displaying short (covalent, 2.655 Å) and long (secondary bonding, 2.830 Å) antimony-sulfur bonds.

Diphenylantimony(III) dithioarsinates, $\text{Ph}_2\text{SbS}_2\text{AsR}_2$ ($\text{R} = \text{Me}$ or Ph), have been synthesised and the structure has been determined for $\text{Ph}_2\text{SbS}_2\text{AsPh}_2$ (**6**). The compound is a dimeric supermolecule formed through $\text{Sb} \cdots \text{S}$ secondary bonds (3.590 and 3.369 Å) longer than the covalent single

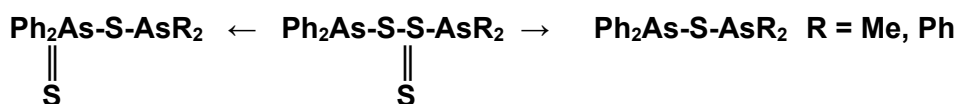
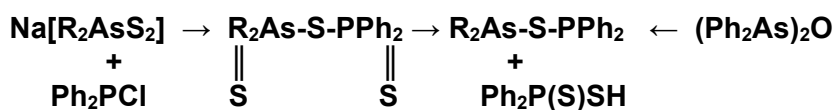
Sb-S bonds (2.486(2) Å. The self-assembly results in the formation of an eight-membered $\text{Sb}_2\text{S}_4\text{As}_2$ ring [23]. An X-ray diffraction analysis showed the $\text{Ph}_2\text{SbS}_2\text{AsMe}_2$ forms a supramolecular chain (**7**) in the crystal *via* bridging dimethyldithioarsinate ligands [17b].



5. VARIOUS REACTIONS INVOLVING DITHIOARSENIC GROUPS

When chlorodiphenylphosphine reacted with sodium dithioarsinates, $\text{Na}[\text{R}_2\text{AsS}_2]$ ($\text{R} = \text{Me}, \text{Ph}$) the products were diorganoarsenic(III) diphenyldithiophosphinates $\text{R}_2\text{AsS-P(S)Ph}$, instead of the expected diphenylphosphinyl dithioarsinates $\text{Ph}_2\text{P-S-As(S)R}_2$, as a result of a rearrangement involving migration of sulfur from arsenic(V) to phosphorus(III) proved by infrared and NMR spectroscopic data. An alternative preparation of the phenyl derivative through the direct reaction of $\text{Ph}_2\text{P(S)SH}$ with $(\text{Ph}_2\text{As})_2\text{O}$ provides additional proof. The reaction was called “sulfotropic rearrangement”) [24].

A similar sulfotropic rearrangement was found for tetraorganodiarsine disulfides, formed in the reaction of chlorodiphenylarsine with sodium dithioarsinates [25]



The oxidation of $(\text{Ph}_2\text{As})_2\text{S}$ with *tert*-butyl hydroperoxide and sulfur in 1:1 and 1:2 molar ratio produces the compounds $\text{Ph}_2\text{As}(\text{S})\text{-S-AsPh}_2$ and $\text{Ph}_2\text{As}(\text{S})\text{-S-As}(\text{S})\text{Ph}_2$, respectively. The dioxidation products are less stable and on recrystallisation an unusual mixed supramolecular adduct $[\text{Ph}_2\text{As}(\text{O})\text{OH}\cdot\text{Ph}_2\text{As}(\text{S})\text{OH}]_2$ self-assembled through hydrogen bonds was isolated [26].

The first oxygen-bridged dithioarsenic(V) compound, $\text{Me}_2\text{As}(\text{S})\text{-O-As}(\text{S})\text{Me}_2$, along with $\text{Me}_2\text{As}(\text{S})\text{-S-As}(\text{O})\text{Me}_2$, was obtained by oxidation of tetramethyldiarsine disulfide $\text{Me}_2\text{As}(\text{S})\text{SAsMe}_2$ with *tert*-butylperoxide. The molecular structure of the oxo-bridged compound was established by single crystal X-ray diffraction. The formation of the oxo-bridged isomer is unexpected and can be rationalized in terms of an oxotropic rearrangement of the sulfur bridged compound. *Ab initio* calculations predict that the oxo-bridged species are more stable than the thio-bridged isomer [27].

The reactions of thioarsinites $\text{R}_2\text{As-SPh}$ ($\text{R} = \text{Me}$ or Ph) with octasulfur in the presence of triethylamine were slow and complex and produced the disulfide $\text{R}_2\text{As}(\text{S})\text{-S-AsR}_2$ mixed with $\text{R}_2\text{As-S-NEt}_3^{(+)}$ and $\text{R}_2\text{As-S}^{(-)}$. The disulfide $\text{Ph}_2\text{As}(\text{S})\text{-S-AsPh}_2$ was not stable and decomposed during work-up to octasulfur and $\text{Ph}_2\text{As-S-AsPh}_2$ which was auto-oxidized to $\text{Ph}_2\text{AsO}_2\text{H}\cdot\text{Ph}_2\text{As}(\text{S})\text{OH}$ [28].

The dimethylarsino dimethyldithioarsinate $\text{Me}_2\text{As}(\text{S})\text{SAsMe}_2$ (also known as "Bunsen's cacodyl disulfide") was prepared from $\text{Me}_2\text{As}(\text{O})\text{OH}$ and hydrogen sulfide or by reaction of dimethylarsine Me_2AsH with excess sulfur. Its molecular structure was established by X-ray diffraction [29, 30].



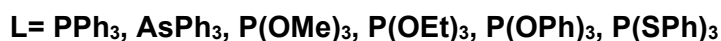
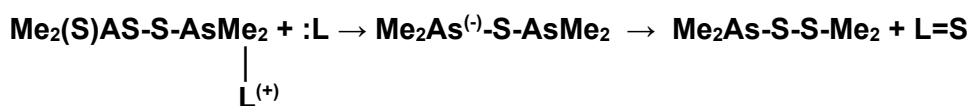
Interesting products were obtained in the reactions of the sulfide $\text{Me}_2\text{As}(\text{S})\text{-S-AsMe}_2$ with various reagents.

The interaction of dimethylarsino dimethyldithioarsinate, $\text{Me}_2(\text{S})\text{As-S-AsMe}_2$, with metal hexacarbonyls under UV irradiation gave complexes of the type $[\text{M}(\text{CO})_5\text{L}]$ ($\text{M} = \text{Cr}$ or W , $\text{L} = \text{Me}_2\text{As-S-AsMe}_2$) and $[\text{MM}'(\text{CO})_{10}\text{L}]$ ($\text{M} = \text{M}' = \text{Cr}$, $\text{L} = \text{Me}_2\text{As-S-AsMe}_2$, and $\text{M} = \text{Cr}$, $\text{M}' = \text{W}$ or $\text{M} = \text{M}' = \text{W}$, $\text{L} = \text{Me}_2\text{As-S-AsMe}_2$). The complex $[\text{Cr}(\text{CO})_5\text{L}]$ decomposes on heating to form $[\text{Cr}(\text{Me}_2\text{As}_2)_3]$ [31].

The reactions of sulfide $\text{Me}_2\text{As}(\text{S})\text{-S-AsMe}_2$ with group 13 halides were studied in detail. With $\text{BF}_3\cdot\text{Et}_2\text{O}$ the product was an equilibrated mixture of $\text{Me}_2\text{As}(\text{S})\text{-S-AsMe}_2$ and $\text{Me}_2\text{As-S-S-AsMe}_2$. While AlCl_3 produced complete isomerisation to $\text{Me}_2\text{As-S-S-AsMe}_2$, the halides GaCl_3 and InCl_3 just formed coordination adducts. With $\text{Tl}(\text{III})$ acetate the unstable complex $(\text{Me}_2\text{AsS}_2)_3\text{Tl}$ formed initially was reduced to the $\text{Tl}(\text{I})$ compound $\text{Me}_2\text{AsS}_2\text{Tl}$ [32].

In the reaction with heavy metal cations in methanol, the disulfide, $\text{Me}_2\text{As}(\text{S})\text{-S-AsMe}_2$, produced insoluble salts (complexes) of dimethyldithioarsinic acid, $\text{Me}_2\text{As}(\text{S})\text{SH}$, and dimethylarsenium ion, $\text{Me}_2\text{As}^{(\cdot)}$ and finally dimethylarsino sulfenium cation, $\text{Me}_2\text{As-S}^{(\cdot)}$. The reactions of $(\text{Me}_2\text{AsS}_2)_x\text{M}$ with triphenylphosphine and trimethyl phosphite gave $\text{Me}_2\text{As-S-AsMe}_2$ and the metal sulfide [33].

The reactions of the disulfide, $\text{Me}_2\text{As}(\text{S})\text{-S-AsMe}_2$ with group 15 Lewis bases was also investigated. Triphenylamine did not react but 4-dimethylaminopyridine and triethylamine isomerised the disulfide to $\text{Me}_2\text{AsSSAsMe}_2$. Triphenylphosphine and $\text{P}(\text{OR})_3$ where (R = Me, Et, Ph) and triphenylarsine desulfurised the disulfide to $\text{Me}_2\text{AsSAsMe}_2$ [34].



With iodine the disulfide $\text{Me}_2\text{As}(\text{S})\text{-S-AsMe}_2$ reacted producing an uncommon compound, dimethylarsinosulfenyl iodide, $\text{Me}_2\text{As-S-I}$, containing a rare sulfur-iodine bond [35].

CONCLUSIONS

The chemistry of dithioarsinates is less popular than that of dithiophosphinates, possibly because of fear of toxicity, unpleasant smell of some compounds and non-commercial availability of most starting materials. The dithioarsinates are less robust than the dithiophosphinates and quite often produce unexpected transformations. In fact this makes them attractive due to the serendipity of their chemistry. The popular belief that the arsenic and phosphorus display a similar chemistry is not entirely true and for this reason the investigation of arsenic compounds, including dithioarsinates, but not limited to, deserves attention on its own.

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