Kirk-Othmer Encyclopedia of Chemical Technology.

ARSENIC COMPOUNDS

Arsenic is the third member of the nitrogen family of elements and hence possesses an outermost shell having the electron configuration of $4s^2 4p^3$. The most common oxidation states of arsenic are -3, $+3$, and $+5$, although compounds containing the simple As^{3-}, As^{3+}, and As^{5+} ions are unknown. In the majority of arsenic compounds the arsenic atom is in the tetrahedral valence state. Compounds in which the arsenic atom is three coordinate are assumed to contain the tetrahedrally hybridized arsenic atom with a lone pair of electrons in one of the hybrid orbitals. Arsenic also forms a number of hypervalent compounds with five or six ligands attached to the central atom. The geometry of such species is generally trigonal–bipyramidal or octahedral. The existence of these compounds has been ascribed to the presence of *d*-orbitals in the valence shell of the arsenic atom. This view has, however, been challenged (1). It has been suggested that the three equatorial ligands in the trigonal–bipyramidal molecules are attached by conventional two-center-two-electron bonds and that the axial ligands are attached by three-center bonds. Participation of *d*-orbitals may slightly stabilize the molecule. Similar reasoning may apply to hypervalent compounds with octahedral geometry.

Arsenic compounds have numerous practical applications. Although a variety of inorganic and organic arsenicals are used in commerce, arsenic trioxide [1327-53-3], As_2O_3, accounted for 98% of the arsenic consumed in 1988 (2).

The commercial uses of arsenic compounds in 1988, measured in terms of elemental arsenic, are wood (qv) preservatives, 69%; agricultural products (herbicides (qv) and desiccants (qv)), 23%; glass (qv), 4%; nonferrous alloys and electronics, 2%; and animal feed additives and pharmaceuticals (qv), 2% (see . Chromated copper arsenate (CCA) [11125-95-4] is the most widely used arsenic-based wood preservative. The Environmental Protection Agency has, however, restricted the use of arsenical wood preservatives to certified applicators.

The principal sources of imported arsenicals by the United States for the years 1986, 1987, and 1988 are shown in Table 1.

The primary world producers of arsenic trioxide for 1988 were Chile, 7,000 t; France, 10,000 t; Sweden, 10,000 t; and Russia, 8,100 t. The December 31, 1988 total world production capacity was 70,000 t. The price of arsenic trioxide (95% pure) in 1986 was $0.726/kg, fob, Tacoma, Washington; the price of Mexican, 99.13% arsenic trioxide in 1986 and 1987 was $0.968/kg, fob, Laredo, Texas.

Arsenic compounds must be considered extremely poisonous. Dust or fumes irritate mucous membranes and lead to arsenical poisoning. When swallowed they irritate the stomach and affect the heart, liver, and kidneys. Nervousness, thirst, vomiting, diarrhea, cyanosis, and collapse are among the symptoms of arsenical poisoning (3). In spite of the toxicity of arsenic compounds, there is evidence that arsenic is an essential nutrient for several animal species (4).

1. Analysis

Although arsenic in quantities in excess of 1 mg can be determined either gravimetrically or titrimetrically, the former method is now seldom used. Arsenic in the +3 oxidation state can be titrated using iodine or potassium

Table 1. Annual Imports of Arsenicals, Metric Tons

	Year		
Exporting country	1986	1987	1988
Canada	1,924	2,012	2,086
Chile	1,659	4,800	6,709
France	6,274	5,341	6,909
Mexico	4,408	4,457	4,187
Sweden	7,069	4,824	3,664
others[a]	4,394	5,409	4,501
Total	*25,728*	*26,843*	*28,056*

[a] Others includes Belgium-Luxembourg, China, Hong Kong, Japan, Philippines, South Africa, and Germany.

bromate, iodate, or permanganate. A number of organic oxidimetric titrating agents have been used. Such reagents are usually *N*-haloamides or *N*-haloimides (see Chloramines and bromamines). Thus bromamine-B (5), chlorobromamine-B (6), bromohydantoin (1-bromo-5,5-dimethylhydantoin) (7), and *N*-chlorosuccinimide (8) are among the compounds suggested for this purpose. Although these titrimetric methods can be adapted to the determination of micro amounts of arsenic, it is more common to determine arsenic colorimetrically, especially in food, by the formation of a diethyldithiocarbamate or molybdenum blue complex (9). Trace amounts of arsenic are usually determined by neutron activation or atomic absorption methods. A detailed description of the determination of arsenic in foods by atomic absorption is available (10). A comparison of the following methods for the determination of traces of arsenic has been made: inductively coupled plasma atomic emission spectrometry, flow injection hydride generation atomic emission spectrometry, graphite furnace atomic absorption, combined furnace–flame atomic absorption, and nondestructive neutron activation (11). For determining arsenic in biological materials, graphite furnace atomic absorption is the most suitable. Another comparison of graphite furnace atomic absorption and neutron activation for the determination of arsenic in biological materials has been reported (12).

2. Inorganic Compounds

2.1. Arsenic Hydrides

Although there are occasionally reports of other arsenic hydrides, eg, As_2H_4, As_2H_2 (or AsH), and As_4H_2, the only well-characterized binary compound of arsenic and hydrogen is arsine.

Arsine [7784-42-1], AsH_3, is a colorless, exceedingly poisonous gas with an unpleasant garliclike odor; mp, $-116.3^\circ C$; bp, $-62.4^\circ C$; density of liquid at $-64.3^\circ C$, 1.640 g/mL; $\Delta H^\circ_{f,298}$ 66.44 kJ/mol (16 kcal/mol); ΔS°_{298} 222.7 J/(mol·K) (53 cal/(mol·K)) (13). It is trigonal pyramidal in shape with $As{-}H$ bond distances of 151.9 pm and $H{-}As{-}H$ bond angles of 91.8°. Arsine is soluble to the extent of 20 mL at 101 kPa (1 atm) per 100 g of water RT. It shows no tendency to accept a proton from water to form an onium ion as does ammonia. At temperatures below $-10^\circ C$ or under pressure, arsine hexahydrate [65423-90-7], $AsH_3{\cdot}6H_2O$, is formed.

Arsine is formed when any inorganic arsenic-bearing material is brought in contact with zinc and sulfuric acid. The arsenides of the electropositive metals are decomposed with the formation of arsine by water or acid. Calcium arsenide [12255-53-7], Ca_3As_2, treated with water gives a 14% yield of arsine. Better yields (60–90%) are obtained by decomposing a solution of sodium arsenide [12044-25-6], Na_3As, in liquid ammonia with ammonium bromide (14, 15). Arsine may be accidentally formed by the reaction of arsenic impurities in commercial acids stored in metal tanks, so that a test should be made for arsine before entry is made into such vessels. It is injurious in 1:20,000 dilution, and a few inhalations may cause death from anoxia or pulmonary edema. Although arsine is toxic to higher living forms, some strains of bacteria and fungi are capable of producing arsine or arsine derivatives.

Arsine is not particularly stable and starts to decompose into its elements well below 300°C. If moisture is present, light effects the decomposition. Arsine is a good reducing agent, capable of reducing many substances. It is not oxidized by air at room temperatures but may be ignited with the formation of arsenic, arsenic trioxide, or arsenic pentoxide, depending upon the supply of air. It reacts with dilute silver nitrate solution with the formation of metallic silver, and with mercuric chloride to give mercuric arsenide [65496-41-5], As_2Hg_3. Chlorine reacts with arsine to give hydrogen chloride and arsenic [7440-38-2]. However, at low temperatures the action of chlorine upon arsine produce chloroarsines, AsH_2Cl and $AsHCl_2$. These are relatively unstable yellow solids (16).

Arsine is used for the preparation of gallium arsenide [1303-00-0], GaAs, (17), and there are numerous patents covering this subject (see Arsenic and arsenic alloys). The conversion of a monomeric arsinogallane to gallium arsenide has also been described (18). Gallium arsenide has important applications in the field of optoelectronic and microwave devices (see Lasers; Microwave technology; photodetectors).

2.1.1. Other Arsenic Hydrides

Diarsine [15942-63-9], As_2H_4, occurs as a by-product in the preparation of arsine by treatment of a magnesium aluminum arsenide alloy with dilute sulfuric acid and also may be prepared by passing arsine at low pressure through an ozonizer-type discharge tube (19). Diarsine is fairly stable as a gas but quite unstable (above $-100°C$) in condensed phases. The ΔH_f° for diarsine is +117 ± 4 kJ/mol (28 ± 1 kcal/mol) and the As—As bond strength is 167 kJ/mol (40 kcal/mol) (19). In addition, two other hydrides of arsenic have been reported but their chemical individuality awaits clarification. Reduction of arsenic(III) compounds by stannous chloride in hydrochloric acid yields a brown amorphous powder corresponding to the formula of arsenic monohydride [14452-84-7], As_2H_2 or AsH (20). The other solid arsenic hydride is reported to be hydrogen diarsenide [65496-40-4], As_4H_2 or As_2H, and is formed by oxidation of arsine with stannic chloride.

2.2. Arsenic Halides

Arsenic forms a complete series of trihalides, but arsenic pentafluoride is the only well-known simple pentahalide. All of the arsenic halides, the physical properties of which are given in Table 2, are covalent compounds that hydrolyze in the presence of water. The trihalides form pyramidal molecules similar to the trivalent phosphorus analogues and may be prepared by direct combination of the elements.

Arsenic trifluoride (arsenic(III) fluoride), AsF_3, can be prepared by reaction of arsenic trioxide with a mixture of sulfuric acid and calcium fluoride or even better with fluorosulfonic acid. Chlorine reacts with ice-cold arsenic trifluoride to produce a hygroscopic solid compound, arsenic dichloride trifluoride [14933-43-8], $AsCl_2F_3$, consisting of $AsCl^+{}_4$ and $AsF^-{}_6$ ions (21). Arsenic trifluoride forms a stable adduct, $2AsF_3{\cdot}3SO_3$, with sulfur trioxide and reacts with nitrosyl fluoride to give nitrosonium hexafluoroarsenate(V) [18535-07-4], $[NO][AsF_6]$.

Arsenic pentafluoride (arsenic(V) fluoride), AsF_5, is a colorless gas that condenses to a yellow liquid; its dielectric constant is 12.8 at 20°C. It is formed by reaction of a mixture of bromine and antimony pentafluoride with arsenic trifluoride. The molecule is a trigonal bipyramid and is somewhat dissociated as indicated by vapor density measurements.

Arsenic trichloride (arsenic(III) chloride), $AsCl_3$, is the most common and important halide of arsenic. It may be formed by spontaneous combination of the elements and, in addition, by the following reactions: (*1*) chlorine with arsenic trioxide; (*2*) sulfur monochloride, S_2Cl^2, or a mixture of S_2Cl_2 and chlorine, with arsenic trioxide; and (*3*) arsenic trioxide with concentrated hydrochloric acid or with a mixture of sulfuric acid and a chloride.

Table 2. Physical Properties of Arsenic Halides

Arsenic halide	CAS Registry Number	Color and physical state at 25°C	Mp, °C	Bp, °C	Specific gravity[a]	Heat of formation, ΔH°_{298}, kJ/mol[b,c]	Entropy, S°_{298}, J/(mol·K)[b,c]
arsenic trifluoride (AsF_3)	[7784-35-2]	colorless liquid	−6.0	62.8	2.666^{0}	−956.25	
arsenic pentafluo-ride (AsF_5)	[7784-36-3]	colorless gas	−79.8	2.8	2.33^{-53}		
arsenic trichloride ($AsCl_3$)	[7784-34-1]	colorless liquid	−16.2	130.2	2.205^{0}	−305	208
arsenic tribromide ($AsBr_3$)	[7784-33-0]	yellow solid	31.2	221	3.66^{15}	−197	363.8[d]
arsenic triiodide (AsI_3)	[7784-45-4]	red solid	140.4	ca 400	4.39^{15}	−58.2	213.0

[a] Temperature, °C, of measurement given as a superscript.

[b] Ref. 13.

[c] To convert J to cal, divide by 4.184.

[d] Gaseous phase.

Arsenic pentachloride [22441-45-8] (arsenic(V) chloride), $AsCl_5$, is produced by irradiation of a solution of $AsCl_3$ in chlorine at $-105°C$ using ultraviolet light (22). Arsenic pentachloride is a pale yellow solid (presumably because of an entrained chlorine impurity) which melts with partial decomposition at $-50°C$. Raman spectra show that it is a trigonal–bipyramidal molecule both in solution and in the solid state.

Arsenic tribromide (arsenic(III) bromide), $AsBr_3$, is similar to the trichloride. The dielectric constant at 35°C is 8.33. The compound is usually made by treating arsenic with a solution of bromine in carbon disulfide.

Arsenic triiodide (arsenic(III) iodide), AsI_3, can be precipitated from a hot solution of trivalent arsenic in hydrochloric acid by the addition of potassium iodide, or it can be formed by treating elemental arsenic with a solution of iodine in carbon disulfide. It is not as easily hydrolyzed as the other arsenic halides, but it decomposes slowly in air at 100°C (rapidly at 200°C) to give a mixture of iodine, arsenic trioxide, and elemental arsenic. Solutions of AsI_3 are unstable, particularly in the presence of moisture.

Also formed by the direct combination of the elements is a red solid compound, arsenic diiodide [13453-17-3], As_2I_4 or AsI_2, which melts at 130°C and dissolves in organic solvents. Treatment of this compound with water causes disproportionation.

$$3\ As_2I_4 \longrightarrow 4\ AsI_3 + 2\ As$$

2.3. Arsenic Oxides and Acids

The only arsenic oxides of commercial importance are the trioxide and the pentoxide. These are readily soluble in alkaline solution, forming arsenites and arsenates, respectively.

Arsenic trioxide [1327-53-3] (arsenic(III) oxide, arsenic sesquioxide, arsenous oxide, white arsenic, arsenic), As_2O_3, is the most important arsenic compound of commerce. The octahedral or cubic modification, arsenolite [1303-24-8], $\Delta H^\circ_{f,298}$, −1313.9 kJ/mol (−314 kcal/mol); $S^\circ C_{298}$, 214 J/(mol·K) (51 cal/(mol·K)), is the most common form and has been known from early times. The monoclinic form, claudetite [13473-03-5], $\Delta H^\circ C_{f,298}$, −1310 kJ/mol (−313 kcal/mol); $S^\circ C_{298}$, 230 J/(mol·K) (55 cal/(mol·K)) (13), is the thermodynamically stable modification consisting of sheets of AsO_3 pyramids sharing oxygen. The octahedral variety is a white solid that sublimes freely above 135°C and melts at 275°C under its own vapor pressure. The octahedral crystal consists of As_4O_6 molecules arranged in a diamond-type lattice. At temperatures above 800°C dissociation to As_2O_3 can be detected, and at 1800°C the molecular weight corresponds to As_2O_3. In nitrobenzene solution the molecular weight corresponds to the formula As_4O_6. Condensation of the vapor above 250°C results usually in the formation of a glassy phase. This is a supercooled liquid which readily devitrifies to form octahedral crystals.

Arsenic trioxide may be made by burning arsenic in air or by the hydrolysis of an arsenic trihalide. Commercially, it is obtained by roasting arsenopyrite [1303-18-0], FeAsS. It dissolves in water to a slight extent (1.7 g/100 g water at 25°C) to form a weakly acidic solution which probably contains the species H_3AsO_3, orthoarsenous acid [36465-76-6]. The oxide is amphoteric and hence soluble in acids and bases. It is frequently used as a primary analytical standard in oxidimetry because it is readily attainable in a high state of purity and is quantitatively oxidized by many reagents commonly used in volumetric analysis, eg, dichromate, nitric acid, hypochlorite, and iron(III).

2.3.1. Arsenous Acids and the Arsenites

Arsenous acid [13464-58-9], AsH_3O_3, is known to exist only in solution. It is a weak acid with a dissociation constant of 8×10^{-16} at 25°C. The free acid apparently has three OH groups attached directly to the arsenic atom and hence is not analogous to phosphorous acid. A number of complex arsenites are known, among which are copper acetate arsenite [12002-03-8], $Cu_2(C_2H_3O_2)(AsO_3)$, Paris green, and cupric hydrogen arsenite [10290-12-7], $CuHAsO_3$, Scheele's green.

Arsenic pentoxide [1303-28-2] (arsenic oxide, arsenic(V) oxide), As_2O_5, is made up of equal numbers of AsO_6 octahedra and AsO_4 tetrahedra sharing corner oxygens to give cross-linked strands (23). The compound is thermally unstable and begins to decompose near the melting point, ca 300°C. The vapor obtained is wholly dissociated into oxygen and arsenic trioxide. The pentoxide can be prepared by reaction of arsenic or of arsenic trioxide with oxygen under pressure. The best method of preparation seems to be the dehydration of crystalline arsenic acid at temperatures above 200°C. Arsenic pentoxide is an oxidizing agent capable of liberating chlorine from hydrogen chloride. It is deliquescent and dissolves only slowly in water, although it is soluble, 230 g/100 g of water at 20°C.

2.3.2. Arsenic Acids and the Arsenates

Commercial arsenic acid, corresponds to the composition, one mole of arsenic pentoxide to four moles of water, and probably is the arsenic acid hemihydrate [7774-41-6], $H_3AsO_4{\cdot}0.5H_2O$. It is obtained by treatment of arsenic trioxide with concentrated nitric acid. Solutions of this substance or of arsenic pentoxide in water behave as triprotic acids with successive dissociation constants: $K_1 = 5.6 \times 10^{-3}$, $K_2 = 1.7 \times 10^{-7}$, and $K_3 = 3.0 \times 10^{-12}$. Hydrated arsenic acid loses water when heated at about 100°C with the formation of pyroarsenic acid [13453-15-1], $H_4As_2O_7$. At higher temperatures additional water is lost to yield metaarsenic acid [10102-53-1], $HAsO_3$. Arsenates derived from each of these acids are known. Treatment of a meta- or pyroarsenate with cold water gives the orthoarsenate.

Arsenates are oxidizing agents and are reduced by concentrated hydrochloric acid or sulfur dioxide. Treatment of a solution of orthoarsenate with silver nitrate in neutral solution results in the formation of a chocolate-brown precipitate of silver orthoarsenate, Ag_3AsO_4, which may be used as a test to distinguish arsenates from phosphates. With hydrofluoric acid, orthoarsenate solutions yield hexafluoroarsenates, eg, potassium hexafluoroarsenate [17029-22-0], $(KAsF_6)_2{\cdot}H_2O$. Arsenates of calcium or lead are used as insecticides; sodium arsenate is used in printing inks and as a mordant.

Arsenous arsenate [12505-65-6] (arsenic dioxide, arsenic tetroxide), As_2O_4, is known and probably corresponds to $As(AsO_4)$.

2.4. Arsenic Sulfides

The physical properties of the common arsenic sulfides are given in Table 3. Numerous arsenic sulfides have been reported as well as compounds containing the $As_3S^+{}_4$ cation [77825-63-9] (24).

Table 3. Physical Properties of Arsenic Sulfides

Arsenic sulfides	CAS Registry Number	Molecular formula	Color and physical state at 25°C	Heat of formation, ΔH_{298}, kJ/mol[a,b]
arsenous sulfide (orpiment)[c]	[12255-89-9]	As_2S_3	yellow solid	−338
arsenic sulfide (realgar)	[12279-90-2]	As_4S_4	red or orange solid	−285
arsenic pentasulfide	[1303-34-0]	As_4S_{10}	yellow solid	
tetraarsenic trisulfide	[1303-41-9]	As_4S_3	orange-yellow	
tetraarsenic pentasulfide	[25114-28-7]	As_4S_5		

[a] Ref. 13.
[b] To convert J to cal, divide by 4.184.
[c] The entropy, $S^\circ{}_{298}$, is 327 J/(mol·K)[b] (13).

Arsenous sulfide (arsenic(III) sulfide, arsenic sesquisulfide, arsenic red), As_2S_3, starts to sublime before melting at 320°C. The bp is 707°C. The solid as well as the vapor consists of discrete molecules similar to those of arsenic trioxide. A red modification is known, but it has not been definitely determined whether this represents another crystal configuration or is because of the presence of impurities. Arsenous sulfide is almost insoluble in water but dissolves in liquid ammonia. It may be prepared by heating arsenic trioxide and elemental sulfur or by passing hydrogen sulfide through a solution of trivalent arsenic in dilute hydrochloric acid. The compound is insoluble in acid, but it dissolves readily in many bases or in alkali metal sulfides to give dithioarsenites, eg, in sodium sulfide solution, sodium dithioarsenite [19102-63-7], $NaAsS_2$ is formed. In polysulfide solutions, arsenous sulfide dissolves forming the thioarsenate ion, $AsS^{3-}{}_4$. Chlorine converts arsenous sulfide to arsenic trichloride and sulfur chloride, S_2Cl_2. Arsenous sulfide burns in air yielding arsenic trioxide and sulfur dioxide; it is oxidized by nitric acid. Arsenic sulfide [65113-28-2], As_4S_6, is also known.

Tetraarsenic trisulfide (dimorphite), As_4S_3, exists in α- and β- modifications. The compound may be synthesized by direct combination of appropriate quantities of the elements. The β- form is stable at room temperature, but changes to the α- form upon heating to 130°C. The As_4S_3 molecule consists of three As atoms in a triangle. Above each arsenic is a sulfur, and then these three sulfur atoms are capped by an arsenic (25–27). As_4S_3 is sparingly soluble in CS_2. If the CS_2 contains some dissolved sulfur, As_4S_3 reacts to form As_4S_4 if the solution is illuminated for a long period of time. The compound forms a broad metastable series of solid solutions with P_4S_3 that contain six different cage molecules (28).

Arsenic sulfide (arsenic monosulfide), As_4S_4, occurs naturally as the mineral realgar. At 267°C it changes into a black allotropic modification; the compound melts at 307°C. The vapor consists of As_4S_4 molecules at 550°C, boils at 565°C, but it begins to dissociate at 800°C, and at 1000°C the molecular weight corresponds to As_2S_2. The compound is made commercially by heating a mixture of iron pyrites and arsenopyrite or by heating arsenic trioxide with sulfur. It is also made by prolonged treatment of arsenous sulfide with boiling aqueous sodium carbonate or by heating a sodium bicarbonate–arsenous sulfide mixture in a sealed tube. It is unaffected by water, but inflames in chlorine, and is oxidized by nitric acid. It is insoluble in hot concentrated hydrochloric acid, but dissolves when warmed with solutions of alkali hydroxides or sulfides with the formation of thioarsenites and some elemental arsenic. The compound is used in pyrotechnics and at times as a depilatory in the leather (qv) industry.

Arsenic pentasulfide (arsenic(V) sulfide), As_4S_{10}, is stable in air up to 95°C, but at higher temperatures begins to dissociate into arsenous sulfide and sulfur. It is prepared by the fusion of arsenic with sulfur followed by extraction with ammonia and reprecipitation at low temperatures by addition of hydrochloric acid. Arsenic pentasulfide is precipitated at low temperatures from strongly acidic arsenate solutions by a rapid stream of hydrogen sulfide. It is hydrolyzed by boiling with water, yielding arsenous acid and sulfur. Salts derived from a number of thioarsenic acids are formed from arsenic pentasulfide and alkali metal sulfides.

2.5. Other Arsenic Compounds

Arsenic trisulfate [65496-42-6], $As_2(SO_4)_3$, may be formed by the treatment of arsenic trioxide with SO_3 at 100°C. Arsenyl sulfate [65423-91-8], $(AsO)_2SO_4$, an easily hydrolyzed, hygroscopic crystalline compound, is formed when arsenic trioxide is dissolved in concentrated sulfuric acid. Arsenic triacetate [5128-94-9], $As(C_2H_3O_2)_3$, mp 82°C, bp 165–170°C, is easily hydrolyzed to a mixture of arsenous and acetic acids.

3. Organic Compounds

Arsenic combines readily with carbon to form a wide variety of compounds containing one or more $As{-}C$ bonds. A number of examples are given in Table 4. These may be broadly divided into As(III) and As(V) compounds. The As(III) compounds contain from one to four organic groups; the As(V) compounds from one to six organic groups. The nomenclature used here, with a few minor exceptions, is that proposed by the International Union of Pure and Applied Chemistry (29). Treatises on organoarsenic compounds are available (30, 31). Two noncritical lists of all organoarsenic compounds prepared or studied between 1937 and 1964 (32) and between 1965 and 1968 (33) have been published. Heterocyclic compounds containing arsenic in the ring are described in two books (34, 35) and several older monographs on organoarsenic compounds exist that are largely of historic interest (36–38).

3.1. Primary and Secondary Arsines

Compared to the vast number of known organoarsenic compounds, relatively few primary ($RAsH_2$) and secondary (R_2AsH) arsines have been described. Primary arsines are commonly prepared by the zinc–hydrochloric acid reduction of substances containing one organic group attached to arsenic (such as arsonic acids, dihaloarsines, and compounds with arsenic—arsenic bonds); the zinc is often amalgamated (39) or coated with copper (40). For example, trifluoromethylarsine [420-42-8], CH_2AsF_3, has been obtained in 98% yield from trifluoromethylarsonous diiodide [353-91-3], CF_3AsI_2, by using copper-coated zinc and hydrochloric acid:

$$CF_3AsI_2 + 2\ H_3O^+ + 2\ Zn \longrightarrow CF_3AsH_2 + 2\ Zn^{2+} + 2\ I^- + 2\ H_2O$$

Good yields of phenylarsine [822-65-1], C_6H_7As, have been obtained by the reaction of phenylarsenic tetrachloride [29181-03-1], $C_6H_5AsCl_4$, or phenyldichloroarsine [696-28-6], $C_6H_5AsCl_2$, with lithium aluminum hydride or lithium borohydride (41). Electrolytic reduction has also been used to convert arsonic acids to primary arsines (42). Another method for preparing primary arsines involves the reaction of arsine with calcium and subsequent addition of an alkyl halide. Thus methylarsine [593-52-2], CH_5As, is obtained in 80% yield (43):

$$Ca + 2\ AsH_3 \xrightarrow[NH_3]{liquid} Ca^{2+} + 2\ AsH_2^- + H_2$$

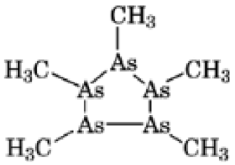
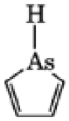
$$CH_3Cl + AsH_2^- \longrightarrow CH_3AsH_2 + Cl^-$$

Secondary arsines, which can be synthesized by methods analogous to those used for primary arsines, are obtained in good yields by the reduction of arsinic acids (44) or haloarsines (45) with amalgamated zinc and hydrochloric acid. They can also be prepared by the alkylation of primary arsenides (46):

$$RAsHLi + RX \longrightarrow R_2AsH + LiX$$

Another good method for preparing secondary arsines involves cleavage of an alkyl or aryl group from a tertiary arsine and subsequent hydrolysis of the resulting secondary arsenide (47, 48):

Table 4. Organic Arsenic Compounds

Compound	CAS Registry Number	Molecular formula	Structural formula
ethylarsine	[593-59-9]	C_2H_7As	$C_2H_5AsH_2$
diethylarsine	[692-42-2]	$C_4H_{11}As$	$(C_2H_5)_2AsH$
triphenylarsine	[603-32-7]	$C_{18}H_{15}As$	$(C_6H_5)_3As$
dimethylbromoarsine	[676-71-1]	C_2H_6AsBr	$(CH_3)_2AsBr$
methyldifluoroarsine	[420-24-6]	CH_3AsF_2	CH_3AsF_2
oxophenylarsine	[637-03-6]	C_6H_5AsO	C_6H_5AsO
phenylarsonous acid	[25400-22-0]	$C_6H_7AsO_2$	$C_6H_5As(OH)_2$
dimethylarsinous cyanide	[683-45-4]	C_3H_6AsN	$(CH_3)_2AsCN$
methyl diphenylarsinite	[24582-54-5]	$C_{13}H_{13}AsO$	$(C_6H_5)_2AsOCH_3$
tetrakis(trifluoromethyl)diarsine	[360-56-5]	$C_4As_2F_{12}$	$(CF_3)_2AsAs(CF_3)_2$
pentamethylpentaarso-lane	[20550-47-4]	$C_5H_{15}As_5$	
4-ethylarsenin	[76782-94-0]	C_7H_9As	
1-chloroarsolane	[30077-24-8]	C_4H_8AsCl	
1*H*-arsole	[4542-21-6]	C_4H_5As	
phenylarsonic acid	[98-05-5]	$C_6H_7AsO_3$	$C_6H_5AsO(OH)_2$
diphenylarsinic acid	[4656-80-8]	$C_{12}H_{11}AsO_2$	$(C_6H_5)_2AsO(OH)$
arsonoacetic acid	[107-38-0]	$C_2H_5AsO_5$	$H_2O_3AsCH_2CO_2H$
diethyl methylarsonate	[14806-25-8]	$C_5H_{13}AsO_3$	$CH_3AsO(OC_2H_5)_2$
triphenylarsine oxide	[1153-05-5]	$C_{18}H_{15}AsO$	$(C_6H_5)_3AsO$
tetrachlorophenylarsorane	[29181-03-1]	$C_6H_5AsCl_4$	$C_6H_5AsCl_4$
tetramethylarsonium perchlorate	[84742-76-7]	$C_4H_{12}AsClO_4$	$(CH_3)_4AsClO_4$
triphenylarsonium 2-propenylide	[88329-28-6]	$C_{21}H_{19}As$	$(C_6H_5)_3As{=}CH{-}CH{=}CH_2$

$$R_3As + 2\ Na \xrightarrow[NH_3]{liquid} R_2AsNa + NaR$$

$$R_2AsNa + H_2O \longrightarrow R_2AsH + Na^+ + OH^-$$

Finally, secondary arsines can be obtained by the reductive cleavage of diarsines with mercury and hydrogen iodide (49) or with lithium aluminum hydride (50).

Methylarsine, trifluoromethylarsine, and bis(trifluoromethyl)arsine [371-74-4], C_2HAsF_6, are gases at room temperature; all other primary and secondary arsines are liquids or solids. These compounds are extremely sensitive to oxygen, and in some cases are spontaneously inflammable in air (45). They readily undergo addition reactions with alkenes (51), alkynes (52), aldehydes (qv) (53), ketones (qv) (54), isocyanates (55), and azo compounds (56). They also react with diborane (43) and a variety of other Lewis acids. Alkyl halides react with primary and secondary arsines to yield quaternary arsenic compounds (57).

3.2. Tertiary Arsines

An enormous number of trialkyl- and triarylarsines are known (32, 33). They are usually prepared by the reaction of an organometallic compound with an arsenic trihalide, a haloarsine, or a dihaloarsine. The Grignard reagent is the organometallic compound most widely employed in these syntheses (58, 59). Organolithium (60), organoaluminum (61), organotin (62), organocadmium (63), and organomercury (64) compounds have also been employed Some triarylarsines (Ar_3As) can be prepared by the sodium-promoted interaction of an aryl halide and an arsenic trihalide (AsX_3) (65):

$$3\ ArX + AsX_3 + 6\ Na \longrightarrow Ar_3As + 6\ NaX$$

This type of reaction is sometimes considered a variant of the Wurtz-Fittig reaction.

Another excellent method for preparing tertiary arsines involves the interaction of a secondary arsenide and an alkyl or aryl halide (66). This method is of particular value in preparing unsymmetrical tertiary arsines (67).

Other methods for preparing tertiary arsines have been employed, but they have limited usefulness. These methods include the cleavage of quaternary arsonium compounds (68), the cyclodehydrohalogenation of haloarsines (69), the reaction of diazonium salts with arsenic trichloride in the presence of a metal such as zinc or iron (70), and the disproportionation of halo- or dihaloarsines (71).

Trimethylarsine [593-88-4], C_3H_9As, has been identified as the toxic volatile arsenical, once known as "Gosio gas," produced by the reaction of certain molds that grow on wallpaper paste and react with inorganic arsenic compounds present in the paper. A number of microorganisms can methylate arsenic trioxide and other arsenic-containing compounds to yield trimethylarsine. These microorganisms include *Scopulariopsis brevicaulis*, *Candida humicola*, and *Gliocladium roseum* (72).

Most trialkylarsines are volatile liquids with intensely disagreeable odors. They react readily with oxygen, and in some cases they ignite spontaneously when exposed to air. Triarylarsines are solids that can usually be handled in air without danger of oxidation. They are, however, easily converted to triarylarsine oxides with suitable oxidizing agents (73).

Tertiary arsines have been widely employed as ligands in a variety of transition metal complexes (74), and they appear to be useful in synthetic organic chemistry, eg, for the olefination of aldehydes (75). They have also been used for the formation of semiconductors (qv) by vapor-phase epitaxy (76), as catalysts or cocatalysts for a number of polymerization reactions (77), and for many other industrial purposes.

3.3. Haloarsines, Dihaloarsines, and Related Compounds

Halo- and dihaloarsines (R_2AsX and $RAsX_2$, where $X =$ Cl or Br) are easily obtained by the reduction of the corresponding arsinic or arsonic acids in hydrochloric or hydrobromic acid. The usual reducing agent is sulfur dioxide catalyzed by iodide ion (78). Iodo- and diiodoarsines are similarly prepared by the reduction of arsinic or arsonic acids with hydriodic acid (79). Dimethylchloroarsine [557-89-1], C_2H_6AsCl, has been obtained by the reduction of dimethylarsinic acid [75-60-5], $C_2H_7AsO_2$, with sodium hypophosphate in hydrochloric acid (80). Fluoro- and difluoroarsines are best prepared from the corresponding chloro- or dichloroarsines by metathesis with an inorganic fluoride. Thus dimethylfluoroarsine [420-23-5], $C_2H_6AsF_2$, has been obtained by the following reaction (81):

$$(CH_3)_2\,AsCl + NH_4F \xrightarrow[85^\circ C]{SbF_3} (CH_3)_2\,AsF + NH_4Cl$$

Other halo- and dihaloarsines can also be prepared by suitable metathetical reactions (82).

The alkylation of arsenic trihalides with organometallic reagents is another method of preparing halo- and dihaloarsines. The metals used in these syntheses include tin (62), cadmium (83), lithium (83), zinc (84), aluminum (85), and magnesium (86). These reactions are not commonly employed because they often give mixtures of haloarsines, dihaloarsines, and tertiary arsines. Good yields of chloro- or bromoarsines can be obtained, however, by the following procedure (86):

$$2\,RMgX + R'_2NAsCl_2 \longrightarrow R_2AsNR'_2 \xrightarrow{HX} R_2AsX$$

A Friedel-Crafts type of reaction between arsenic trichloride and diarylamines or diaryl ethers is a good method of preparing certain heterocyclic chloroarsines (34, 35, 87). For example, a good yield of 10-chloro-5,10-dihydrophenarsazine [578-94-9], $C_{12}H_9AsClN$, often known as Adamsite, is obtained by refluxing a mixture of diphenylamine and arsenic trichloride for several hours. Although this chloroarsine is a solid, it can be dispersed in air in the form of minute particles and employed as a chemical warfare agent (see Chemicals in war). 2-Chlorovinyldichloroarsine [541-25-3], $C_2H_2AsCl_3$, is obtained in admixture with the corresponding chloroarsine and tertiary arsine by the interaction of acetylene and arsenic trichloride in the presence of a catalyst such as aluminum chloride or mercuric chloride (88). The common name for this dichloroarsine is Lewisite. It is an extremely toxic vesicant and has been proposed as a chemical warfare agent.

Dihalo- and haloarsines are very reactive substances. They are readily oxidized by halogens to compounds of the types $RAsX_4$ or R_2AsX_3 (89). Hydrolysis of dihaloarsines yields either arsonous acids, $RAs(OH)_2$, or their anhydrides, $(RAsO)_x$ (90). Methyloxoarsine, $(CH_3AsO)_x$, has been found to act as an oxygen transfer agent (91). Thus it reacts with compounds of the type $[C_5(CH_3)_5M(CO)_2]_2$, where M is Mo or W and $C_5(CH_3)_5$ is pentamethylcyclopentadienyl, to form the neutral metal-oxo clusters $[C_5(CH_3)_5]_2W_6O_{17}$ and $[C_5(CH_3)_5]_6Mo_8O_{16}$. Haloarsines on hydrolysis give arsinous acids, R_2AsOH, or their anhydrides, $(R_2As)_2O$ (92). In addition, dihalo- and haloarsines react with Grignard or lithium reagents to give tertiary arsines (93), with certain reducing agents to give primary or secondary arsines (41, 42), with alcohols or alkoxides to give esters (94), with amines to give aminoarsines (95), with thiols to give sulfides, often known as thioarsenites (96), and with selenols to give selenides (97). They also undergo metathetical reactions with ammonium or metallic halides (81, 82), pseudohalides (98), and carboxylates (99).

3.4. Diarsines and Diarsenes

Under certain conditions, the reduction of compounds with two organic groups attached to arsenic may give rise to tetraalkyl-or tetraaryldiarsines. Thus a number of diarsines have been obtained by the reduction of arsinic acids with phosphorous or hypophosphorous acid (100). Diarsines can also be prepared by the treatment of a metal dialkyl- or diarylarsenide with iodine (101) or a 1,2-dihaloethane (102).

Diarsines are extremely reactive compounds. Tetramethyldiarsine (cacodyl) [471-35-2], $C_4H_{12}As_2$, and tetraethyldiarsine [612-08-8], $C_8H_{20}As_2$, are spontaneously flammable in air. Tetraallyldiarsine is said to explode violently on being dropped into oxygen (103). Tetraphenyldiarsine [2215-36-31], $C_{24}H_{20}As_2$, is not spontaneously flammable in air. It does, however, react essentially quantitatively with moist air to give diphenylarsinic acid [4656-80-8], $C_{12}H_{11}AsO_2$, and bis(diphenylarsenic) oxide [34262-48-1], $C_{24}H_{20}As_2O$ (104):

$$2\ (C_6H_5)_2\,AsAs\,(C_6H_5)_2 + 2\ O_2 + H_2O \longrightarrow 2\ (C_6H_5)_2\,AsO_2H + (C_6H_5)_2\,AsOAs\,(C_6H_5)_2$$

Unlike many distibines and dibismuthines, diarsines do not appear to exhibit thermochromic effects (105).

Although the preparation of diarsenes, the arsenic analogues of azo compounds, was first claimed during the nineteenth century, it was not until 1983 that such a compound was unequivocally characterized (106). It was obtained in good yield by the base-promoted interaction of a primary arsine and a dichloroarsine, both of which were sterically hindered:

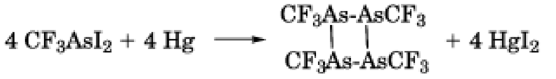
$$2,4,6\text{–}(t\text{–}C_4H_9)_3C_6H_2AsH_2 + [(CH_3)_3Si]_2CHAsCl_2 + 2\ \mathrm{DBU} \xrightarrow{\mathrm{THF}}$$

$$2,4,6\text{–}(t\text{–}C_4H_9)_3C_6H_9)_3C_6H_2As{=}AsCH[Si(CH_3)_3]_2 + 2\ \mathrm{DBU{\cdot}HCl}$$

where $\mathrm{DBU} =$ 1,5-diazabicyclo[5.4.0]undec-5-ene. The arsenic—arsenic distance in the diarsene is 0.22 nm, the shortest such distance ever reported.

3.5. Cyclic and Polymeric Substances Containing Arsenic—Arsenic Bonds

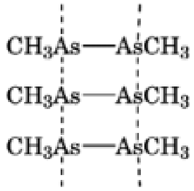
A number of organoarsenic compounds containing rings of four, five, or six arsenic atoms have been prepared (cyclic polyarsines). The first such four-membered ring compound to be adequately characterized, tetrakis (trifluoromethyl) tetrarsetane [7547-15-1], was obtained by the interaction of a diiodoarsine and mercury (107, 108):



Other compounds containing rings of four or five arsenic atoms can be prepared by the treatment of dichloroarsines with sodium (109). The compound $(C_6H_5As)_6$, once known as arsenobenzene [20738-31-2], is readily synthesized by the reduction of phenylarsonic acid with hypophosphorous acid (110). This substance contains a six-membered ring of arsenic atoms arranged in the chair form. The $\mathrm{As{—}As}$ distances are 0.24 nm, and the $\mathrm{As{—}As{—}As}$ angles average 91°. The phenyl groups are arranged equatorially. The preparation of pentamethylpentaarsolane [20550-47-4], $(CH_3As)_5$, by two different methods has been described (111).

Cyclic polyarsines undergo a number of reactions with transition metal compounds to form complexes containing both $\mathrm{As{—}As}$ and $\mathrm{As{—}metal}$ bonds. The structural chemistry of these complexes has been the subject of a recent review (112).

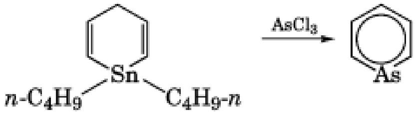
A large number of polymeric substances, $(RAs)_x$ or $(ArAs)_x$, are also known (113). They are usually prepared by the reduction of arsonic acids with hypophosphorous acid (100, 114) or sodium dithionite (115). Most of these polymers have not been well characterized. An insoluble, purple material, poly(methylarsinidene) [26403-94-1], $(CH_3As)_x$, prepared by the interaction of methylarsine and a dihalomethylarsine, however, has been shown by an x-ray investigation to have a ladderlike polymeric structure in which the inter-rung distances correspond to one-electron bonds (116):



The substance appears to be a semiconductor with pronounced photoconductive properties (117).

3.6. Arsenin and Its Derivatives

Arsenin (arsabenzene) [289-31-6], C_5H_5As, the arsenic analogue of pyridine, can be prepared by the treatment of 1,4-dihydro-1,1-dibutylstannabenzene with arsenic trichloride (118):



A large number of arsenin derivatives have also been studied. The potential aromaticity of this ring system has aroused considerable interest and has been investigated with the aid of nmr, uv, photoelectron, and microwave spectroscopy as well as by *ab initio* molecular orbital calculations (119). Arsenin does possess aromatic character.

3.7. Arsonic and Arsinic Acids

The arsonic acids, compounds of the type $RAsO(OH)_2$, are among the most important organic arsenicals. The aliphatic arsonic acids are generally prepared by the Meyer reaction; ie, heating an alkyl halide with As_4O_6 in alkaline solution:

$$As\,(ONa)_3 + RX \longrightarrow RAsO\,(ONa)_2 + NaX$$

Where X is Br or Cl, the free acids may be obtained by acidification of the alkaline solution, but where X is I, the acids must be isolated as salts to avoid reduction of the arsonic acids by HI. Rather than using alkyl halides, alkyl or dialkyl sulfates or alkyl arenesulfonates can be used. Primary alkyl halides react rapidly and smoothly, secondary halides react only slowly, whereas tertiary halides do not give arsonic acids. Allyl halides undergo the Meyer reaction, but vinyl halides do not. Substituted alkyl halides can be used; eg, ethylene chlorohydrin gives 2-hydroxyethylarsonic acid [65423-87-2], $C_2H_7AsO_4$. Arsinic acids, $R_2AsO(OH)$, are also readily prepared by substituting an alkali metal arsonite, $RAs(OM)_2$, for sodium arsenite:

$$RAs\,(ONa)_2 + R'X \longrightarrow RR'As\,(O)\,ONa + NaX$$

A number of long-chain dialkylarsinic acids have been prepared by the following series of reactions (120):

$$R_2NAsCl_2 + 2\,R'MgX \longrightarrow R'_2AsNR_2 + MgCl_2 + MgX_2$$

$$R'_2AsNR_2 + H_3O^+ \longrightarrow R'_2AsOH + R_2NH^+{}_2$$

$$R'_2AsOH + H_2O_2 \longrightarrow R'_2AsO_2H + H_2O$$

Aromatic arsonic acids are generally prepared by the Bart reaction from an aromatic diazonium salt and sodium arsenite:

$$ArN_2X + As(ONa)_3 \longrightarrow ArAsO(ONa)_2 + N_2 + NaX$$

A number of substituted phenylarsonic acids have been prepared by means of the Bart reaction (121). For the preparation of arsinic acids a sodium arylarsonite is used, and mixed diaryl or alkylarylarsinic acids can be prepared:

$$ArN_2X + RAs(ONa)_2 \longrightarrow ArRAs(O)ONa + N_2 + NaX$$

The Bart reaction is successful with a wide variety of aromatic and heterocyclic amines. A variation in which an aromatic amine, in the presence of arsenic trichloride, is diazotized in an organic solvent (the Scheller reaction) has also found wide application. Both arsonic and arsinic acids can be prepared by the Scheller reaction which often gives better yields than the Bart reaction with electron-attracting substituents on the aromatic ring. For the commercial preparation of 4-aminophenylarsonic acid [98-50-0] (arsanilic acid), $C_6H_8AsNO_3$, and 4-hydroxyphenylarsonic acid [98-14-6], $C_6H_7AsO_4$, the Béchamp reaction is used:

$$C_6H_5NH_2 + AsO(OH)_3 \longrightarrow 4{-}H_2NC_6H_4AsO(OH)_2 + H_2O$$

$$C_6H_5OH + AsO(OH)_3 \longrightarrow 4{-}HOC_6H_4AsO(OH)_2 + H_2O$$

Although the yields in the Béchamp reaction are not large, the starting materials can be recovered and recycled. In addition to aniline, substituted anilines such as 2-, 3-, and 4-methylanilines, 2- and 4-chloroanilines, and 2- and 4-nitroanilines have been arsonated under the conditions of the Béchamp reaction. Similarly, 2- and 3-methylphenol give the 3-methyl-4-hydroxyphenylarsonic acid and 2-methyl-4-hydroxyphenylarsonic acid [26738-23-8], $C_7H_9AsO_4$. By-products of the Béchamp reaction are the corresponding arsinic acids. Thus from aniline, bis(4-aminophenyl)arsinic acid [6309-25-7], $C_{12}H_{13}AsN_2O_2$, and from phenol, bis(4-hydroxyphenyl)arsinic acid are formed. Under high temperature conditions the arsinic acids become the principal products of the reaction.

Arsonic and arsinic acids have found a number of industrial uses. They have been used as corrosion inhibitors for iron and steel, additives to motor fuel, agricultural bactericides, herbicides, and fungicides. 3-Nitro-4-hydroxyphenylarsonic acid (roxarsone) [121-19-7], $C_6H_6AsNO_6$, has found widespread use as an additive to poultry feed for the control of coccidiosis and other poultry diseases (122, 123). Arsanilic acid [98-50-0], $C_6H_8AsNO_3$, has also been used for this purpose (124) and for growth promotion in swine. It is manufactured and supplied by Duphar Nutrition Co., Inc., Fleming Laboratories, Inc., Dr. Mayfield Laboratories, Inc., and Whitmoyer Laboratories, Inc. 4-Nitrophenylarsonic acid [98-72-6], $C_6H_6AsNO_5$ and 4-[(aminocarbonyl)amino]phenylarsonic acid (carbarsone) [121-59-5], $C_7H_9AsN_2O_4$, have been used as additives to turkey feed to control histomoniasis and to improve feed efficiency. Both monosodium methylarsonate (MSMA) [2163-80-6], and disodium methylarsonate (DSMA) [144-21-8] have been widely used as selective herbicides, particularly for the control of crabgrass in established turf and for grassy weeds in cotton fields. In 1986 the U.S. consumption of MSMA was 2,700 metric tons and of DSMA was 900 metric tons. A mixture of dimethylarsinic acid (cacodylic acid) and its sodium salt [59164-68-0] have been used as herbicides and for the defoliation of cotton. Over one thousand metric tons of cacodylic acid were consumed in the United States in 1986. In 1987 the United States exported 490 metric tons of cacodylic acid and its salts.

Both arsonic and arsinic acids give precipitates with many metal ions, a property which has found considerable use in analytical chemistry. Of particular importance are certain azo dyes (qv) containing both arsonic and sulfonic acid groups which give specific color reactions with a wide variety of transition, lanthanide, and actinide metal ions. One of the best known of these dyes is 3,6-bis[(2-arsonophenyl)azo]-4,5-dihydroxy-2,7-naphthalenedisulfonic acid [1668-00-4], $C_{22}H_{18}As_2N_4O_{14}S_2$, generally called Arsenazo III. This compound forms stable inner complexes with certain metal ions enabling spectrophotometric determination in strong acid solution. A number of other azo-substituted arsonic acids have been introduced. A review article has been written on the use of these compounds (125).

A number of esters of arsonic and arsinic acids have been prepared. One method involves the oxidation of dialkyl alkylarsonites with selenium dioxide:

$$\mathrm{RAs\,(OR')_2 \xrightarrow{SeO_2} RAs\,(O)\,(OR')_2}$$

A better method involves the use of silver salts of arsonic acids:

$$\mathrm{RAs\,(O)\,(OAg)_2 + 2\,R'X \longrightarrow RAs\,(O)\,(OR')_2 + 2\,AgX}$$

Finally, both arsonic and arsinic acids can be esterified directly using the appropriate alcohol by removal of the water formed in the esterification. Azeotropic distillation using benzene or toluene is generally used for this purpose. On heating slowly, arsonic acids form anhydrides, $(RAsO_2)_n$. Thioarsonic acids, $RAsS(SH)_2$, and thioarsinic acids, $R_2AsS(SH)$, are unknown, but sodium salts, $RAsS(SNa)_2$ and $R_2AsS(SNa)$ have been prepared. Esters of the type $R(C_6H_5)AsS(OR')$ have been prepared by heating alkyl arsinites with sulfur (126):

$$\mathrm{R\,(C_6H_5)\,AsOR' + S \longrightarrow R\,(C_6H_5)\,AsS\,(OR')}$$

3.8. Arsine Oxides

Both aliphatic and aromatic arsine oxides, compounds of the type R_3AsO, are well known. These compounds have been prepared by the oxidation of trialkylarsines using mercury(II) oxide or 30% hydrogen peroxide, with the rigid exclusion of oxygen (127). The products, which are purified by sublimation, are extremely hygroscopic and can only be handled under dry box conditions. The aromatic arsine oxides are generally prepared by the alkaline hydrolysis of dihaloarsoranes, R_3AsX_2, or by oxidation of triarylarsines using potassium permanganate, hydrogen peroxide, or iodine. Mixed aliphatic-aromatic arsine oxides, eg, $(C_6H_5)_2CH_3AsO$ (127), diethylphenylarsine oxide [17767-98-5], $C_6H_5(C_2H_5)_2AsO$, (63) and $C_6H_5(C_2H_5)As(O)CH_2CO_2H$ [32295-95-7] (128), have also been prepared. When dihaloarsoranes are hydrolyzed under alkaline conditions, hydrated compounds are obtained. These were at one time considered to be dihydroxides, $Ar_3As(OH)_2$. X-ray studies on the triphenyl compound, however, have shown that this exists as a dimer $[(C_6H_5)_3AsO{\cdot}H_2O]_2$, with each AsO group hydrogen bonded to two water molecules and each water molecule bonded to two AsO groups (129). The hydrolysis of dihaloarsoranes under milder conditions (aqueous ethanol or aqueous acetone) gives compounds which are usually listed as hydroxyhalides, $R_3As(OH)X$. These can also be prepared by the action of hydrohalic acids on arsine oxides. In addition to the halides, compounds of the type $R_3As(OH)Y$, where Y is NO_3, HSO_4, or ClO_4, are known. Chlorohydroxytriphenylarsenic [15736-85-3], $(C_6H_5)_3As(OH)Cl$, and bromohydroxytriphenylarsenic [15736-84-2], $(C_6H_5)_3As(OH)Br$, have been shown by x-ray diffraction to possess the structure $(C_6H_5)_3AsO{-}{-}{-}H{-}{-}{-}X$, with very short hydrogen bonds (130). Most of these compounds are weak electrolytes in acetonitrile, but the perchlorate is a strong electrolyte in this solvent (131). With strong acids, $HClO_4$, HBF_4, CF_3CO_2H, and $HSbCl_6$, compounds of the type $[(C_6H_5)_3AsO]_2HY$ can be prepared (132, 133). The arsine oxides are Lewis bases and form coordination compounds with transition and actinide metal compounds. Solutions of arsine oxides in nitromethane are useful for extracting salts of U(VI), Pu(IV), Pu(VI), Np(IV), and Np(VI) from nitric acid solutions of these elements (134, 135). The arsine oxides form 1:1 adducts with a variety of phenols (136).

Trialkyl- and triarylarsine sulfides have been prepared by several different methods. The reaction of sulfur with a tertiary arsine, with or without a solvent, gives the sulfides in almost quantitative yields. Another method involves the reaction of hydrogen sulfide with a tertiary arsine oxide, hydroxyhalide, or dihaloarsorane. X-ray diffraction studies of triphenylarsine sulfide [3937-40-4], $C_{18}H_{15}AsS$, show the arsenic to be tetrahedral; the arsenic–sulfur bond is a true double bond (137). Triphenylarsine sulfide and trimethylarsine sulfide [38859-90-4], C_3H_9AsS, form a number of coordination compounds with salts of transition elements (138, 139). Both trialkyl- and triarylarsine selenides have been reported. The trialkyl compounds have been prepared by refluxing trialkylarsines with selenium powder (140). The preparation of triphenylarsine selenide [65374-39-2], $C_{18}H_{15}AsSe$, from dichlorotriphenylarsorane and hydrogen selenide has been reported (141), but other workers could not duplicate this work (140).

3.9. Haloarsoranes

Halides of the types $RAsX_4$, R_2AsX_3, R_3AsX_2, and R_4AsX are known. The R_4AsX compounds are ionic in nature and are discussed under arsonium salts. The tetrahalides are unstable compounds which frequently decompose on standing and are readily hydrolyzed in moist air to form arsonic acids. Aryltetrachloroarsoranes are readily prepared from aryldichloroarsines in an atmosphere of dry chlorine (142). Tetrafluorophenylarsorane [650-44-2], $C_6H_5AsF_4$, has been prepared from phenylarsonic acid and sulfur tetrafluoride (143):

$$C_6H_5AsO_3H_2 + 3\ SF_4 \longrightarrow C_6H_5AsF_4 + 3\ SOF_2 + 2\ HF$$

The ^{19}F nmr spectrum of this compound gives only one signal over a wide range of temperatures, a result attributed to Berry pseudorotation (144). No alkyl- or aryltetrabromoarsorane has been reported. There is, however, an early report on the preparation of tetraiodomethylarsorane from methylarsonic acid and hydriodic acid (145).

Dialkyl- and diaryltrihaloarsoranes are more stable than the tetrahalo compounds, but can be readily decomposed at comparatively low temperatures. The trichloro compounds are usually prepared by the action of chlorine on dialkyl- or diarylchloroarsines. Tribromodiphenylarsorane [38338-43-1], $C_{12}H_{10}AsBr_3$, has been prepared by means of a bromodiphenylarsine [3095-87-2], $C_{12}H_{10}AsBr$, intermediate (146). The starting material is diphenyl(phenylthio)arsine [15367-57-4], $C_{18}H_{15}AsS$:

$$(C_6H_5)_2\,AsSC_6H_5 + Br_2 \longrightarrow (C_6H_5)_2\,AsBr + C_6H_5SBr$$

$$(C_6H_5)_2AsBr + Br_2 \longrightarrow (C_6H_5)_2AsBr_3$$

No triiodoarsorane has been reported. Trifluorodiphenylarsorane [2357-18-8], $C_{12}H_{10}AsF_3$, has been prepared by several methods. One method involves the reaction of benzene with arsenic pentafluoride and subsequent treatment of the resulting salt with cesium fluoride (147):

$$2\ C_6H_6 + 2\ AsF_5 \longrightarrow \left[(C_6H_5)_2\,AsF_2\right]\ \left[AsF_6\right] + 2\ HF$$

$$[(C_6H_5)_2AsF_2]\ [AsF_6] + CsF \longrightarrow (C_6H_5)_2AsF_3 + CsAsF_6$$

It has also been prepared from diphenylarsinic acid and sulfur tetrafluoride (147), and by the direct fluorination of diphenylarsine [829-83-4] using fluorine diluted with argon.

Trialkyl- and triaryldihaloarsoranes have been studied to a much greater extent than the tri- and tetrahaloarsoranes. The dihalo compounds are stable crystalline species, although they decompose on heating:

$$R_3AsX_2 \xrightarrow{\Delta} R_2AsX + RX$$

The usual method of preparing these compounds is by direct halogenation of tertiary arsines. Other halogenating agents, eg, lead tetrachloride or sulfuryl chloride, have also been used. Although the difluorides have been prepared by direct fluorination using fluorine diluted with argon (148), they are usually prepared from the dibromides or dichlorides by reaction with silver fluoride. Mixed diarylalkyl- and aryldialkyldihaloarsoranes are also well known. When iodine or bromine is used in excess, tetrahalides of the type R_3AsX_4 are obtained. These compounds are ionic in the solid state and are strong electrolytes in acetonitrile solution. Dibromo- and dichlorotriphenylarsoranes react with interhalogens to form such compounds as $[(C_6H_5)_3AsCl][ICl_2]$ [76002-28-31], $[(C_6H_5)_3AsCl][ICl_4]$ [76002-97-1], and $[(C_6H_5)_3AsCl][IBr_2]$ [76002-28-3]. The structure of the dihaloarsoranes R_3AsX_2 varies with the nature of both R and X. Thus, trimethyldifluoroarsorane [64811-88-7], $C_3H_9AsF_2$, and trimethyldichloroarsorane [17756-06-8], $C_3H_9AsCl_2$, contain pentacovalent arsenic as shown by conductivity measurements and infrared spectra, and they appear to be trigonal bipyramids. Dibromotrimethylarsorane [17756-09-1], $C_3H_9AsBr_2$, is a stronger electrolyte than the dichloro compound in acetonitrile. Spectroscopic evidence is in accord with an ionic structure for this compound (149). Diiodotrimethylarsorane [17756-08-0], $C_3H_9AsI_2$, and diiodotriphenylarsorane [3964-45-2], $C_{18}H_{15}AsI_2$, are both strong electrolytes in acetonitrile solution. It has been concluded that the high conductance of the triphenyl compound results from disproportionation of the following type (150):

$$2\,(C_6H_5)_3AsI_2 \rightleftharpoons (C_6H_5)_3As + (C_6H_5)_3AsI^+ + I_3^-$$

The strong conductance of the trimethyl compound may be because of a similar disproportionation.

In addition to the trialkyl- and triaryldihaloarsoranes there are a number of compounds of the type R_3AsY_2, where Y is a pseudohalide, nitrate, carboxy, or other negative group. They are usually prepared from trialkyl- or triaryldibromo- or dichloroarsoranes by metathesis. Thus diazidotrimethylarsorane [21121-84-6], $C_3H_9AsN_6$, has been prepared in the following manner (151):

$$(CH_3)_3\,AsCl_2 + 2\,NaN_3 \longrightarrow (CH_3)_3\,As\,(N_3)_2 + 2\,NaCl$$

Dinitratotriphenylarsorane [18513-99-0], $C_{18}H_{15}AsN_2O_6$, has similarly been obtained from dibromotriphenylarsorane and silver nitrate (152):

$$(C_6H5)_3\,AsBr_2 + 2\,AgNO_3 \longrightarrow (C_6H_5)_3\,As\,(NO_3)_2 + 2\,AgBr$$

The nitrato compound is a weak electrolyte in acetonitrile solution.

3.10. Arsonium Salts

Arsonium salts are compounds of the type R_4AsY, where R may be either an alkyl or aryl group and Y is a wide variety of negative groups, such as halogen, nitrate, sulfate, and perchlorate. Both triaryl- and trialkylarsines are readily quaternized by treatment with an alkyl halide. Thus triphenylarsine and methyl bromide give methyltriphenylarsonium bromide [14002-59-6], $C_{19}H_{18}AsBr$ (153). The order of increasing reactivity of alkyl halides is $Cl < Br < I$ and primary > secondary > tertiary. Tetraphenylarsonium bromide [507-27-7], $C_{24}H_{20}AsBr$, is prepared from triphenylarsine oxide and phenylmagnesium bromide (154). Another method involves the reaction of triphenylarsine, bromobenzene, and anhydrous aluminum chloride. Potassium iodide is added to the reaction mixture so that the product is isolated as tetraphenylarsonium iodide [7422-32-4], $C_{24}H_{20}AsI$ (155). Arsonium salts other than halides can be readily obtained from the halides by reaction of the appropriate reagent. For example, reaction of arsonium halides with acids such as nitric or perchloric acids yields arsonium nitrates or perchlorates, respectively. Another method involves the reaction of an arsonium hydroxide with the appropriate acid. Arsonium salts can also be obtained by the cleavage of pentaalkyl or pentaarylarsenic compounds. Thus reaction of pentaphenylarsorane [19376-61-5], $C_{30}H_{25}As$, with excess chlorine, bromine, or iodine gives the corresponding tetraphenylarsonium trihalides and halobenzenes. Pentaarylarsenic compounds react with hydrohalic acids to yield tetraarylarsonium halides and aryl halides (156).

Arsonium salts have found considerable use in analytical chemistry. One such use involves the extraction of a metal complex in aqueous solution with tetraphenylarsonium chloride in an organic solvent. Titanium(IV) thiocyanate [35787-79-2] (157) and copper(II) thiocyanate [15192-76-4] (158) in hydrochloric acid solution have been extracted using tetraphenylarsonium chloride in chloroform solution in this manner, and the Ti(IV) and Cu(II) thiocyanates determined spectrophotometrically. Cobalt, palladium, tungsten, niobium, and molybdenum have been determined in a similar manner. In addition to their use for the determination of metals, anions such as perchlorate and perrhenate have been determined as arsonium salts. Tetraphenylarsonium permanganate is the only known insoluble salt of this anion.

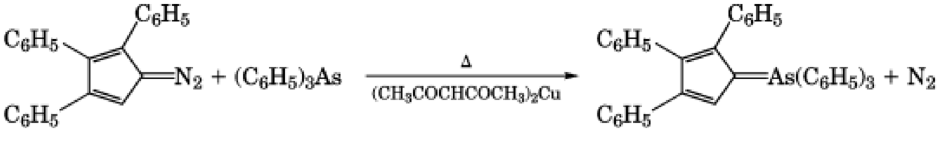
Arsonium halides containing one or more alkyl groups lose an alkyl halide on pyrolysis to give a tertiary arsine. This reaction has been used for the synthesis of compounds containing arsenic as a member of the heterocyclic ring. For example, pyrolysis of trimethyl-4-(1,7-dibromoheptyl)arsonium bromide, $[(CH_3)_3AsCH(CH_2CH_2CH_2Br)_2]Br$, resulted in the loss of three moles of methyl bromide and the formation of 1-arsabicyclo[3.3.0]octane [4432-50-2], $C_7H_{13}As$ (159)

3.11. Arsonium Ylides

Arsonium ylides were first prepared by reaction between an arsonium halide and phenyllithium. Thus methyltriphenylarsonium iodide [1499-33-8], $C_{19}H_{18}AsI$, and phenyllithium give triphenylarsonium methylide [19365-61-8], $C_{19}H_{17}As$:

$$\left[(C_6H_5)_3\,AsCH_3\right]I + C_6H_5Li \longrightarrow (C_6H_5)_3\,As{=}CH_2 + LiI + C_6H_6$$

In this case the ylide was not isolated but allowed to react with benzophenone to give, after hydrolysis with hydrochloric acid, 1,1-diphenylethylene, diphenylacetaldehyde, and triphenylarsine (160). An excellent method for preparing arsonium ylides involves the reaction between a stable diazo compound and triphenylarsine in the presence of a copper catalyst such as bis(acetylacetonato)copper(II) (161). Rather than a diazo compound, an iodonium ylide can be used; again a copper catalyst is necessary for an optimum yield of product. An example of the use of a diazo compound is shown in the formulation of triphenylarsonium 2,3,4-triphenylcyclopentadienylide [29629-32-1], $C_{41}H_{31}As$:



Arsenic ylides of the types $R_3As{=}CH_2$ and $R_3As{=}CHR'$ are unstable and generally react with carbonyl compounds to give either a tertiary arsine and an epoxide, or a mixture of these two compounds and the normal Wittig reaction products (an alkene and a tertiary arsine oxide). By contrast, arsenic ylides, such as those of the type $R_3AsCHC(O)R'$, are stable and react with carbonyl compounds to give the normal Wittig reaction products. It has been shown, however, that the method used in preparing the ylide can influence the subsequent reaction with a carbonyl compound. Thus, the two ylides, $(C_6H_5)_3As{=}CHC_6H_5$ and $(C_6H_5)_3As{=}CHC_6H_4Cl$-4, when prepared by two different methods, gave only the normal Wittig products with carbonyl compounds when prepared by one method, and only an epoxide and triphenylarsine when prepared by the other method (162). Arsenic ylides react several hundred times more rapidly than phosphorus ylides in the Wittig reaction. Furthermore, arsenic ylides often react with carbonyl compounds that do not react with phosphorus ylides. For this reason arsenic ylides are frequently preferred for the Wittig reaction (163).

3.12. Pentaalkyl- and Pentaarylarsoranes

Compounds of the type R_5As, where R may be aliphatic or aromatic, have assumed considerable importance in arsenic chemistry. Pentamethylarsorane [51043-92-6], $C_5H_{15}As$, has been prepared from dichlorotrimethylarsorane [17756-06-8], $C_3H_9AsCl_2$, and two equivalents of methyllithium in dimethyl ether solution at $-60^\circ C$ (164). It is stable in air and only slowly hydrolyzes to tetramethylarsonium hydroxide [34618-96-7], $C_4H_{13}AsO$, and methane. Pentaphenylarsorane [19376-61-5], $C_{30}H_{25}As$, has been prepared by the reaction of phenyllithium with tetraphenylarsonium bromide [507-27-7], $C_{24}H_{20}AsBr$, triphenylarsine oxide [1153-05-5], $C_{18}H_{15}AsO$ or 4-methyl-phenyliminotriphenylarsorane [65423-89-4], 4-$CH_3C_6H_4N{=}As(C_6H_5)_3$. Although only a few pentaalkylarsoranes have been described in the chemical literature, a large number of pentaarylarsoranes have been prepared, including a number of spirocyclic compounds. These compounds are of particular interest in studies on the stereochemistry of five-covalent compounds (165).

3.13. Arsenic Compounds Used in Medicine

Arsenic compounds have been employed as therapeutic agents for at least 2400 years (166, 167). During the fifth century BC, Hippocrates recommended the use of an ointment containing arsenic sulfide (probably realgar) for the treatment of ulcers. Galen (138–201 AD) and various Roman authors prescribed similar arsenic preparations for skin diseases, tuberculosis, asthma, and leprosy. The great Persian physician, Avicenna, believed that arsenic compounds were valuable for the treatment of a number of infectious diseases. During the Middle Ages, arsenic trioxide (white arsenic) was extensively used both by physicians and by professional poisoners. However, at the close of the twentieth century, the therapeutic use of inorganic arsenicals must be considered obsolete.

Modern work on arsenical drugs can be said to have started in 1905; it was demonstrated that sodium hydrogen 4-aminophenylarsonate (Atoxyl) [127-85-5] could cure experimental trypanosomiasis (168). This finding prompted a systematic study of the chemical and biological properties of aromatic arsenicals (169). Using Atoxyl as a starting material, about a thousand organic derivatives of arsenic were prepared during a period of ten years. This research led to several drugs that can cure syphilis.

By 1932 a total of 12,500 compounds of arsenic had been synthesized and some had been clinically tested. Since 1943, when penicillin was shown to be effective for the therapy of syphilis (170) (see Antibiotics, β-lactams, penicillin and others), there has been much less work on the use of organoarsenic compounds in medicine. No important new arsenical drug has been introduced. However, arsenicals are still important for the treatment of African trypanosomiasis (166, 171–173); they are probably indispensable for the late neurological stage of the disease (see Antiparasitic agents-anthelmintics). Toxic reactions caused by arsenicals can often be successfully treated using 2,3-dimercapto-1-propanol (dimercaprol, BAL) [59-52-9], $C_3H_8OS_2$.

Melarsoprol (Mel B, arsobal) [494-79-1], $C_{12}H_{15}AsN_6OS_2$, is a thioarsenite that is active against human trypanosomiasis caused by *T. gambiense* or *T. rhodesiense*, and it has been successfully employed for the treatment of infections of the nervous system (171–173). It often causes toxic effects, however, and it should be employed only under strict medical supervision (173). The drug is much too toxic for prophylactic use. Another disadvantage is that trypanosomes are becoming resistant to melarsopol (172). In the United States this drug is available only from the Centers for Disease Control, Atlanta, Georgia.

Melarsonyl potassium (Mel W, Trimelarsen) [13355-00-5] is a thioarsenite closely related to melarsoprol, and it also has been used for the treatment of trypanosomiasis (172). However, it appears to be more toxic and less effective than melarsoprol. The only advantage of melarsonyl potassium is that it is water-soluble and can be administered intramuscularly or subcutaneously. This property is useful when the intravenous route cannot be employed.

Carbarsone (Amebarsone) was once widely used for the treatment of intestinal amebiasis. Like other arsonic acids, however, carbarsone may cause skin rashes and even damage to the vision. Although it is still available for medicinal use, it is really obsolete as an amebicide because less toxic and more effective nonarsenicals are now available (174).

Arsenamide (thiacetarsamide) [531-72-6], $C_{11}H_{12}AsNO_5S_2$, is a thioarsenite that is employed in veterinary medicine.Although relatively toxic, it has proved useful for the treatment of *Dirofilaria immitis* (heartworm) infestation in dogs (175). It is in fact the only drug recommended for killing the adult worms associated with this disease. It should not be used, however, in critically ill dogs.

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