BISMUTH COMPOUNDS

1. Introduction

Bismuth is the fifth member of the nitrogen family of elements and, like its congeners, possesses five electrons in its outermost shell, $6s^2 6p^3$. In many compounds, the bismuth atom utilizes only the three $6p$ electrons in bond formation and retains the two 6*s* electrons as an inert pair. Compounds are also known where bismuth is bonded to four, five, or six other atoms. Many bismuth compounds do not have simple molecular structures and exist in the solid state as polymeric chains or sheets.

The +3 oxidation state is exhibited by bismuth in the vast majority of its compounds. A few inorganic and a variety of organic compounds, however, contain the element in the +5 state. Other rarer oxidation states reported for bismuth include +2, +1, and −3. Bismuth also forms polynuclear ionic species with oxidation states that are usually fractional and range from −1 to +1.

Technical information concerning bismuth and its compounds is distributed periodically by the Bismuth Institute, a nonprofit organization incorporated in La Paz, Bolivia, that has an information center in Brussels. Information on the production and consumption of bismuth is available from the U.S. Geological Survey Minerals Yearbook on the World Wide Web. World production of bismuth in 2000 stands at ~4000 tons/year. Major applications of bismuth compounds include pharmaceuticals (eradicating, eg, *Helicobacter pyloris*, a bacteria inflicting ulcers), additives to ceramics, plastics, catalysts for use in industrial organic chemistry, pigments in cosmetics (BiOCl), and paints (Bi-vanadate colors). Metallic bismuth is widely used in metallurgy (steel additives, fusible alloys etc). Ecological considerations favor applications of bismuth because it is considered nontoxic and noncarcinogenic notwithstanding its heavy metal status.

2. Analysis

Dissolution of Bi in various environments for analytical purposes is effected by digestion with HNO_3 or HNO_3/H_2SO_4. Separations from interfering substances are achieved by extraction with dithizone and cupferron (1) or ion exchange separations. Gravimetric methods for the determination of bismuth involve weighing as $BiPO_4$, BiOCl, or Bi_2O_3 (2). The best general method for determining macro and semimicro quantities of bismuth is the direct titration of bismuth, using the disodium salt of ethylenediaminetetraacetic acid (EDTA) (3). The method is fast, convenient, and accurate. Few foreign ions in moderate amounts interfere. The titration is best carried out at a pH between 1.5 and 2.0. When the end point is detected by photometric methods, the titration of bismuth as dilute as 10^{-6} M is feasible.

Trace amounts of bismuth in ores or in nonferrous alloys can be determined with photometric methods using reagents such as dithizone, thiourea, potassium iodide, or dimercaptothiopyrone (4). Atomic absorption spectrometry (AAS) is most frequently used for the analyses of low concentrations of Bi in a variety of samples including ores and concentrates, superconductors, geological and biological materials (5). Bismuth can be determined by AAS by using flame, hydride generation (HG), electrothermal (ET) atomization, and other methods. Detection limits of 50 ng/mL, 0.2 ng/mL, and 4 pg of Bi have been reported for flame AAS, HG AAS, and GF AAS, respectively. Extremely low concentrations of Bi (detection limit 0.4 pg/mL) can be determined by the technique of inductively coupled plasma mass spectrometry (ICP MS) (5).

3. Inorganic Compounds of Bismuth

3.1. Bismuthine. Bismuthine, BiH_3, [18288-22-7], is a colorless gas, unstable at room temperature, but isolatable as a colorless liquid at lower temperatures. Owing to its instability and difficulty of preparation, no more than a few hundred milligrams of the pure compound have been available for any single study. Vapor pressure data from −116 to −43°C have been determined, and by extrapolation, a normal boiling point of +16.8°C has been indicated; ΔH_v, calculated from the same data, is 25.15 kJ/mol (6.01 kcal/mol) (6). Experimental quantities are best prepared by disproportionation of either methylbismuthine, CH_3BiH_2, [66172-95-0] or dimethylbismuthine, $(CH_3)_2BiH$ [14381-45-4] (6):

$$(CH_3)_{3-n}BiH_n \longrightarrow n/3BiH_3 + (3-n)/3(CH_3)_3Bi \qquad (1)$$

In the case of methylbismuthine, the disproportionation occurs upon keeping the compound at −45°C for several hours; 389.1 mg of methylbismuthine yields 241.1 mg of BiH_3.

At room temperature, bismuthine rapidly decomposes into its elements. The rate of decomposition increases markedly at higher temperatures (7). Bismuthine decomposes when bubbled through silver nitrate or alkali solutions but is unaffected by light, hydrogen sulfide, or 4 *N* sulfuric acid solution. There is no evidence for the formation of BiH_4^+, though the methyl derivative, $(CH_3)_4Bi^+$, is known. The existence of BiH_4^+ would not be anticipated on the basis of the trend found with other Group 15 “onium” ions.

3.2. Bismuthides. Many intermetallic compounds of bismuth with alkali metals and alkaline earth metals have the expected formulas M_3Bi and M_3Bi_2, respectively. These compounds are not salt-like but have high coordination numbers, interatomic distances similar to those found in metals, and metallic electrical conductivities. They dissolve to some extent in molten salts (eg, NaCl−NaI) to form solutions that have been interpreted from cryoscopic data as containing some Bi^{3-}. Both the alkali and alkaline earth metals form another series of alloy-like bismuth compounds that become superconducting at low temperatures (Table 1). The MBi_2 compounds are particularly noteworthy as having extremely short bond distances between the alkali metal atoms.

3.3. Bismuth Halides. Bismuth forms subhalides that have or approximate the composition BiX, trihalides, BiX_3 and a single pentahalide, BiF_5.

Table 1. **Alloy-like Superconducting Bismuth Compounds**

Compound	CAS Registry Number	Formula	Temperature, K[a]
lithium bismuthide	[12048-27-0]	LiBi	2.47
sodium bismuthide	[12258-63-8]	NaBi	2.22
potassium dibismuthide	[12431-17-3]	KBi_2	3.58
rubidium dibismuthide	[55127-10-1]	$RbBi_2$	4.25
cesium dibismuthide	[12233-24-8]	$CsBi_2$	4.75
calcium tribismuthide	[66271-89-4]	$CaBi_3$	1.7
strontium tribismuthide	[12589-81-0]	$SrBi_3$	5.62
barium tribismuthide	[12047-02-8]	$BaBi_3$	5.69

[a] Temperature below which the compound is superconducting.

Bismuth Subhalides. Vapors above solutions of a bismuth trihalide in molten bismuth contain the species BiX and/or $(BiX)_n$, where X = Cl, Br, or I (8). At temperatures <323°C, a black, diamagnetic, orthorhombic solid of the overall composition $BiCl_{1.167}$ may be isolated from solutions of bismuth trichloride in molten bismuth. The crystal structure consisting of bismuth cluster cations and two different bismuth chloroanions corresponds to the formula $[(Bi_9{}^{5+})_2(BiCl_5{}^{2-})_4(Bi_2Cl_8{}^{2-})]$ (9). The bromo analogue $BiBr_{1.167}$ (10) has a similar structure. Bismuth also forms true crystalline mono halides, BiBr (10) and BiI (11), which have polymeric mixed-valent structures, $[Bi(0)Bi(II)X_2]_n$.

Bismuth Trihalides. Reaction of bismuth trioxide with aqueous HF, HCl, or HBr or direct halogenation of metallic bismuth in the case of Cl_2, Br_2, I_2 yields the corresponding bismuth trihalides. Physical and thermochemical properties of the more important bismuth halides appear in Table 2.

Bismuth Trifluoride. Bismuth(III) fluoride is a white to gray-white powder, density 8.3 g/mL, that is essentially isomorphous with orthorhombic YF_3, requiring nine-coordination about the bismuth (19). It has been suggested that BiF_3 is best considered an eight-coordinate structure with the deviation from the YF_3 structure resulting from stereochemical activity of the bismuth lone-pair of electrons. In accord with its structure, the compound is more ionic than the other bismuth halides. It is almost insoluble in water ($5.03 \pm 0.05 \times 10^{-3}$ M at pH 1.15) and dissolves only to the extent of 0.010 g/100 g of anhydrous HF at 12.4°C.

Bismuth trifluoride is usually prepared by dissolving either Bi_2O_3 or BiOF in hydrofluoric acid to yield the addition compound bismuth trifluoride trihydrofluoride $BiF_3 \cdot HF$ or $H_3(BiF_6)$, [66184-11-0]. Careful evaporation of the solution permits isolation of a gray solid, which upon heating loses HF to yield BiF_3. It may be purified by sublimation in a stream of HF at 500°C. Bismuth trifluoride may also be prepared by (*1*) reaction of Bi_2O_3 with sulfur tetrafluoride, SF_4; (*2*) treatment of metallic bismuth with HF at 350°C; and (*3*) reduction of BiF_5 in a dilute stream of hydrogen. Bismuth trifluoride is not readily hydrolyzed even by boiling water. However, addition of HF causes the formation of $BiF_3 \cdot 3HF$, which is readily hydrolyzed to bismuth oxyfluoride, BiOF, [13520-72-4]. Heating BiF_3 at 200–300°C in air results in the formation of some oxide or oxyfluoride. Between 600 and 800°C fluorine is gradually replaced by oxygen yielding phases such as $BiO_{0.1}F_{2.8}$, BiOF, and, on prolonged heating (60 h at 670°C), Bi_2O_3. The so-called cubic phase of BiF_3 probably contains some oxygen.

Complexes of BiF_3 are almost unknown, but crystallization from a hot solution of ammonium fluoride that has been saturated with freshly precipitated bismuth trioxide yields crystals of ammonium tetrafluorobismuthate(III), NH_4BiF_4, [13600-76-5]. This complex is readily decomposed by water.

Bismuth Trichloride. Bismuth(III) chloride is a colorless, crystalline, deliquescent solid made up of pyramidal molecules (20). The nearest intermolecular Bi–Cl distances are 0.3216 and 0.3450 nm. The density of the solid is 4.75 g/mL and that of the liquid at 254°C is 3.851 g/mL. The vapor density corresponds to that of the monomeric species. The compound is monomeric in dilute ether solutions, but association occurs at concentrations > 0.1 M. The electrical conductivity of molten $BiCl_3$ is of the same order of magnitude as that found for ionic substances.

Table 2. **Physical Properties of Bismuth Compounds**

Bismuth compound	CAS Registry Number	Formula	mp, °C	bp, °C	$\Delta H^\circ_{f,298}$, kJ/mol[a]	S°_{298}, J/mol · K[a]	$\Delta H^\circ_{\mathrm{fusion}}$, kJ/mol[a]	$\Delta S^\circ_{\mathrm{fusion}}$, J/mol · K[a]	$\Delta H^\circ_{\mathrm{subl},298}$, kJ/mol[a]	$\Delta S^\circ_{\mathrm{subl},298}$, J/mol · K[a]	Bi–X bond energy, kJ/mol[a]	Reference
bismuth trifluoride	[7787-61-3]	BiF_3	649[b]	900 ± 10	−900 ± 13	123 ± 4	21.6 ± 0.6	23.4 ± 0.8	201 ± 3	195 ± 3	381	12
bismuth pentafluoride	[7787-62-4]	BiF_5	151	230								
bismuth trichloride	[7787-60-2]	$BiCl_3$	233.5	44.7	−379	174 ± 6	23.9		114 ± 1	183 ± 2	279	13,14
bismuth monochloride	[14899-70-8]	BiCl			−131	94.5					300 ± 4	13,15
bismuth oxychloride	[7787-59-9]	BiOCl			−367	120						13
bismuth tribromide	[7787-58-8]	$BiBr_3$	219	441	−276 ± 2	190 ± 1	21.8		115 ± 1	182 ± 1	233.0 ± 1.4	16
bismuth triiodide	[7787-64-6]	BiI_3	408.6	542[c]	−151 ± 4	224.8 ± 0.8	39.1 ± 0.3	57.3 ± 0.4	134.3 ± 0.5	183.4 ± 0.8	181 ± 5	17,18
bismuth trioxide	[1304-76-3]	Bi_2O_3[d]	824		−574	151.5						13
bismuth trisulfide	[1345-07-9]	Bi_2S_3	850		−143	200						13
bismuth tritelluride	[1304-82-1]	Bi_2Te_3			−77.4	260.9						13

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

[b] The mp frequently cited is 120°C higher than this and is, apparently, for material contaminated with oxyfluoride.

[c] The normal bp has been extrapolated from vapor-pressure data.

[d] Monoclinic.

Bismuth trichloride is usually prepared by chlorination of the molten metal or by dissolving bismuth metal in aqua regia; evaporation of the solution yields the bismuth trichloride dihydrate, $BiCl_3{\cdot}2H_2O$ [66172-88-1], and upon distillation, it decomposes to give anhydrous bismuth trichloride. The commercial product frequently is not anhydrous. Bismuth trichloride shows considerable tendency to form addition compounds. Reaction with ammonia yields the colorless, easily volatilized bismuth trichloride triammine, $BiCl_3{\cdot}3NH_3$, [66172-89-2] as well as the red, thermally unstable bismuth trichloride hemiammine, $2BiCl_3{\cdot}NH_3$, [66172-90-5]. Compounds of formula $BiCl_3{\cdot}NO$, $BiCl_3{\cdot}2NO_2$, and $BiCl_3{\cdot}NOCl$ may be isolated; these are stable in dry air but are decomposed by moisture. Bismuth trichloride is soluble in organic solvents like diethyl ether, acetone, or trimethyl amine; solution is presumably accompanied by the formation of complexes between the organic donor molecules and $BiCl_3$ as acceptor. Recently, complexes of $BiCl_3$ with dimethylsulfoxide (dmso) (21), tetrahydrofuran (thf) (22), bipyridine (bpy) (23), phenantroline (24), bis(diphenylphosphino)methane (24), or crown ethers (25) have been characterized by X-ray crystallography. Also complexes between $BiCl_3$ (or $BiBr_3$) and aromatic hydrocarbons, like benzene, mesitylene, or paracyclophanes have been prepared. Usually the aromatic ring adopts a centroid η^6-coordination on the bismuth center (26). A number of complex bismuth halides are also well known, eg, disodium bismuth pentachloride, Na_2BiCl_5, [66184-10-9]; sodium dibismuth heptachloride, $NaBi_2Cl_7$, [66184-09-6]; and trisodium bismuth hexachloride, Na_3BiCl_6, [66114-82-7]. The acid, hydrogen dibismuth heptachloride trihydrate, $HBi_2Cl_7{\cdot}3H_2O$, [66124-39-9] is a crystalline substance, stable at room temperature, that may be isolated by cooling a solution of $BiCl_3$ in concentrated hydrochloric acid to 0°C. Also other polynuclear anions, eg, $Bi_2Cl_{11}{}^{5-}$, $Bi_4Cl_{18}{}^{6-}$, $Bi_8Cl_{13}{}^{6-}$ are known (27).

Bismuth Tribromide. Bismuth(III) bromide is a hygroscopic, golden-yellow, crystalline solid that exists in two modifications, α-$BiBr_3$ stable below and β-$BiBr_3$ above 158°C. The structure of the former consists of trigonal pyramidal $BiBr_3$ molecules with Bi–Br 2.66 Å and three intermolecular contacts Bi···Br 3.32 Å per bismuth atom (28). The high temperature modification, β-$BiBr_3$ is polymeric with Bi in octahedral holes of a kind of hexagonal dense packing of the Br atoms (28).

Bismuth tribromide may be prepared by dissolving Bi_2O_3 in excess concentrated hydrobromic acid. The slurry formed is allowed to dry in air, then gently heated in a stream of nitrogen to remove water, and finally distilled in a stream of dry nitrogen. Bismuth tribromide is soluble in aqueous solutions of KCl, HCl, KBr, and KI but is decomposed by water to form bismuth oxybromide, BiOBr, [7787-57-7]. It is soluble in acetone and ether, and practically insoluble in alcohol. It forms complexes with NH_3 and dissolves in hydrobromic acid from which dihydrogen bismuth pentabromide tetrahydrate, $H_2BiBr_5{\cdot}4H_2O$, [66214-38-8], may be crystallized at −10°C. Polynuclear bromobismuthates, eg, $Bi_2Br_{10}{}^{4-}$ or $Bi_4Br_{16}{}^{4-}$ (27) and complexes of $BiBr_3$ with N- (23), P- (29), O- (30), or S- (31) donor ligands are also known.

Bismuth Triiodide. Bismuth(III) iodide is a greenish black crystalline powder. The iodines are in a hexagonal close-packed array with each bismuth having six nearest-neighbor iodines at 0.32 nm (32). This suggests that the lone pair on bismuth is stereochemically inactive and that the compound is largely ionic in character.

Bismuth triiodide may be prepared by heating stoichiometric quantities of the elements in a sealed tube. It undergoes considerable decomposition at 500°C and is almost completely decomposed at 700°C. However, it may be sublimed without decomposition at 3.3 kPa (25 mmHg). Bismuth triiodide is essentially insoluble in cold water and is decomposed by hot water. It is soluble in absolute alcohol (3.5 g/100 g), benzene, toluene, xylene and in liquid ammonia, in which it forms a red triammine complex. It dissolves in hydroiodic acid solutions from which hydrogen tetraiodobismuthate(III), $HBiI_4 \cdot 4H_2O$, [66214-37-7] may be crystallized, and it dissolves in potassium iodide solutions to yield the red compound, potassium tetraiodobismuthate(III), $KBiI_4$, [39775-75-2]. Compounds of the type tripotassium bismuth hexaiodide, K_3BiI_6, [66214-36-6] salts with polynuclear or polymeric anions, eg, $Bi_3I_{12}{}^{3-}$ or $(BiI_4)_n{}^{n-}$ (27) and complexes of BiI_3 with $OP[N(CH_3)_2]_3$ (33) are also known.

Bismuth Pentafluoride. Bismuth(V) fluoride consists of long white needles that have been shown to have the same structure as the body-centered, tetragonal α-polymorph of uranium hexafluoride. The density of the solid is 5.4 g/mL at 25°C. The solid consists of infinite chains of trans-bridged BiF_6 polyhedra; dimers and trimers are present in the vapor phase (34). Bismuth pentafluoride may be prepared by the fluorination of BiF_3 or metallic bismuth at 600°C. For purification, it may be separated from BiF_3 by repeated sublimation at 120°C. At higher temperatures it decomposes to yield BiF_3 and fluorine.

Bismuth pentafluoride is an active fluorinating agent. It reacts explosively with water to form ozone, oxygen difluoride, and a voluminous chocolate-brown precipitate, possibly a hydrated bismuth(V) oxyfluoride. A similar brown precipitate is observed when the white solid compound bismuth oxytrifluoride, $BiOF_3$, [66172-91-6], is hydrolyzed. Upon standing, the chocolate-brown precipitate slowly undergoes reduction to yield a white bismuth(III) compound. At room temperature BiF_5 reacts vigorously with iodine or sulfur; $> 50°C$ it converts paraffin oil to fluorocarbons; at 150°C it fluorinates uranium tetrafluoride to uranium pentafluoride; and at 180°C it converts Br_2 to bromine trifluoride, BrF_3, and bromine pentafluoride, BrF_5, and chlorine to chlorine fluoride, ClF. It apparently does not react with dry oxygen.

Treatment of BiF_5 with BrF_3 results in the formation of fluorobromonium hexafluorobismuthate(V), $[BrF_2][BiF_6]$, [36608-81-8], which may be isolated as white hygroscopic crystals upon removal of excess BrF_3 under vacuum. This compound is relatively stable but at reduced pressures undergoes decomposition to BrF_3 and BiF_5. Adducts are formed between BiF_5 and the fluorides of lithium, sodium, potassium, or silver by heating equimolar quantities of the respective compounds to 85–150°C. The resulting hexafluorobismuthate(V) compounds are more stable to reduction than BiF_5. The X-ray diffraction pattern of potassium hexafluorobismuthate(V), $KBiF_6$, [26914-71-6], is similar to that of potassium hexafluoroantimonate(V), $KSbF_6$, [16893-92-8]. Silver hexafluorobismuthate(V), $AgBiF_6$, [66184-08-5], may also be formed by warming elemental silver and $[BrF_2][BiF_6]$ dissolved in BrF_3. This compound is hygroscopic, soluble in HF, and reacts with water to form a chocolate-brown precipitate and probably some ozone.

3.4. Bismuth Oxide Halides. Hydrolysis of a bismuth trihalide yields the corresponding bismuth(III) oxide halide (oxyhalide). Bismuth oxyfluoride, BiOF, [13520-72-4], and bismuth oxyiodide, BiOI, [7787-63-5], may also be formed by heating the corresponding bismuth trihalide in air. When either bismuth oxychloride [7787-59-9] or bismuth oxybromide, BiOBr, [7787-57-7] is heated >700°C, complex bismuth oxyhalides of composition $Bi_{24}O_{31}X_{10}$ are formed. Bismuth oxychloride, BiOCl, is a white, lustrous, crystalline powder (density, 7.72 g/mL) that is practically insoluble in water, alcohol, acids, and bases. Hot concentrated alkali solutions convert it to bismuth trioxide. It is used in fingernail polishes, lipsticks, and face powders to give a nacreous effect. A study (35) in which rats were fed 1, 2, or 5% BiOCl for 2 years showed no carcinogenic or toxic effects. Bismuth oxybromide, a white, amorphous powder, and bismuth oxyiodide, a brick-red, amorphous powder having a density of 7.92 g/mL, are essentially insoluble in water, alcohol, acids, and bases and have been used in the manufacture of dry-cell cathodes.

3.5. Bismuth Oxides and Bismuthates. The only oxide of bismuth that has been definitely isolated in a pure state is bismuth trioxide. An acidic oxide that approximates the composition Bi_2O_5 certainly exists. However, there is considerable question as to the exact nature of this material and the species involved. A number of other oxides have been reported, eg, bismuth oxide (1:1) [1332-64-5], bismuth oxide (1:2), bismuth oxide (2:4) [12048-50-9], bismuth oxide (3:5), and bismuth oxide (4:9), but the evidence for their existence as chemical entities is meager at best.

Bismuth Trioxide. Bismuth(III) oxide [1304-76-3] has a complicated polymorphism. At times some of the reported phases deviate from Bi_2O_3 by having too little or too much oxygen; at least in one instance, because of the ready contamination of Bi_2O_3 melts with silicon, the reported phase probably has the composition of bismuth oxide silicate, $Si_2Bi_{24}O_{40}$, [66256-73-3]. The common oxide, α-Bi_2O_3, is a pale-yellow, monoclinic solid, density $= 9.32 \pm 0.02$ g/mL, which is stable up to 710°C. Half of the bismuth atoms are five-coordinate, and half are six coordinate. The lone-pair electrons on bismuth presumably occupy the sixth position for the five-coordinate bismuth and are responsible for the distortion of the oxygen about the six-coordinate bismuth (36).

Bismuth trioxide may be prepared by the following methods: (*1*) the oxidation of bismuth metal by oxygen at temperatures between 750 and 800°C; (*2*) the thermal decomposition of compounds such as the basic carbonate, the carbonate, or the nitrate (700–800°C); (*3*) precipitation of hydrated bismuth trioxide upon addition of an alkali metal hydroxide to a solution of a bismuth salt and removal of the water by ignition. The gelatinous precipitate initially formed becomes crystalline on standing; it has been represented by the formula $Bi(OH)_3$ and called bismuth hydroxide [10361-43-0]. However, no definite compound has been isolated. Bismuth trioxide is practically insoluble in water; it is definitely a basic oxide, and hence dissolves in acids to form salts. Acidic properties are just barely detectable, eg, its solubility slightly increases with increasing base concentration, presumably because of the formation of bismuthate(III) ions, such as $Bi(OH)_6{}^{3-}$ and related species.

Bismuth trioxide forms numerous, complex, mixed oxides of varying composition when fused with CaO, SrO, BaO, and PbO. If high purity bismuth, lead, and copper oxides and strontium and calcium carbonates are mixed together with metal ratios Bi:Pb:Sr:Ca:Cu = 1.9:0.4:2:2:3 or 1.95:0.6:2:2:3 and calcined at 800–835°C, the resulting materials have the nominal composition $Bi_{1.9}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ and $Bi_{1.95}Pb_{0.6}Sr_2Ca_2Cu_3O_x$ and become superconducting at ~110 K (37). Also lead free high Tc superconducting Bi-Sr-Ca-Cu-O oxides (38,39) are known.

3.6. Higher Oxides of Bismuth and Related Compounds. Oxidation of either a fused mixture of sodium oxide and bismuth trioxide or a suspension of bismuth trioxide in 40–50% sodium hydroxide solution yields a product in which much of the bismuth is apparently in the +5 oxidation state. Air or oxygen are suitable oxidizing agents for the molten mixture; sodium hypochlorite, chlorine, bromine, or sodium persulfate may be used for the aqueous suspension. The reactions are favored by excess alkali, and though >90% of the bismuth is oxidized to the pentacovalent state, the product is contaminated with considerable excess alkali. Extraction with methanol at 0°C removes the excess alkali and yields pure sodium metabismuthate(V), $NaBiO_3$, [12232-99-4]. Addition of nitric or perchloric acid produces a material ranging in composition from Bi_2O_4 to Bi_2O_5, which slowly loses oxygen. This material and sodium metabismuthate(V) are very good oxidizing agents. The sodium bismuthate of commerce varies in color from yellow to brown to black. It has about two molecules of water per bismuth atom and is insoluble in water. It is capable of oxidizing manganese(II) compounds in nitric acid solution to permanganate, a reaction commonly used as a qualitative test for manganese. $NaBiO_3$ oxidizes Fe^{3+} in basic medium to $FeO_4{}^{2-}$.

3.7. Sulfides and Related Compounds. Bismuth(III) sulfide, [1345-07-9], bismuth sesquisulfide, Bi_2S_3, is a dark-brown to grayish black crystalline solid, mp 850°C and density of 6.78 g/mL. It occurs naturally as the mineral bismuth glance and is isostructural with stibnite, Sb_2S_3. It may be prepared by heating sulfur and bismuth or by the addition of a soluble sulfide to an aqueous solution of bismuth(III). It is almost insoluble in water or alkaline solutions but dissolves in concentrated nitric acid or hot concentrated hydrochloric acid. Concentrated alkali metal sulfide solutions or melts dissolve Bi_2S_3 to yield crystalline compounds such as potassium thiobismuthate(III), $KBiS_2$, [12506-13-7]. These compounds are rapidly oxidized in air; similar compounds of silver, copper, and lead occur naturally. Fusion of Bi_2S_3 with a bismuth halide yields air-stable compounds, bismuth chlorosulfide, BiClS, [19264-19-8], bismuth bromosulfide, BiBrS, [14794-86-6], and bismuth iodosulfide, BiIS [15060-32-9]. Other mixed halide sulfide compounds have been reported: bismuth bromide sulfide $Bi_{19}S_{27}Br_3$, (19:3:27) [51185-13-8], has been shown to consist of $(Bi_4S_6)_\infty$ chains in which bismuth atoms in neighboring chains are linked by bromide ions (40). Bismuth disulfide, BiS_2, [12323-18-1], can be prepared at 5000 MPa at 1250°C. The compound is a soft, gray, needlelike, crystalline solid. Bismuth trisulfide has been used as a high temperature lubricant and has been of interest for its photo- and thermoelectric properties.

Related Compounds. Bismuth triselenide, Bi_2Se_3 [12068-69-8] and bismuth tritelluride, Bi_2Te_3, [1304-82-1], are known, and in addition to the stoichiometric compounds, preparations can be made containing excess Bi, Se, or Te. Compounds are also known in which some of the Te in Bi_2Te_3 is replaced by S or Se and some of the Se in Bi_2Se_3 by S, eg, dibismuth ditellurium selenide, Bi_2Te_2Se [12010-72-9] and dibismuth ditellurium sulfide, Bi_2Te_2S [1304-78-5]. All of these materials are of interest for their semiconducting properties.

3.8. Bismuth Salts. Bismuth trioxide dissolves in concentrated solutions of strong oxyacids to yield bismuth salts. In more dilute solutions of strong acids or in solutions of weak acids, the oxide reacts to form bismuthyl or basic salts. The normal salts are very susceptible to hydrolysis.

Bismuth Triperchlorate Pentahydrate. Bismuth(III) perchlorate pentahydrate, $Bi(ClO_4)_3{\cdot}5H_2O$ [66172-92-7], is prepared by dissolving Bi_2O_3 in 70% $HClO_4$. Anhydrous bismuth triperchlorate, $Bi(ClO_4)_3$, [14059-45-1] may be prepared by heating bismuthyl perchlorate monohydrate, $BiOClO_4{\cdot}H_2O$ [66172-93-8] between 80 and 100°C. Attempts to dissolve bismuth metal in concentrated perchloric acid have resulted in explosions. Treatment of bismuth or Bi_2O_3 with dilute solutions of perchloric acid yields hydrates of bismuthyl perchlorate.

Bismuth Trinitrate Pentahydrate. Bismuth(III) nitrate pentahydrate, $Bi(NO_3)_3{\cdot}5H_2O$ [10035-06-0] is obtained by dissolving bismuth metal, Bi_2O_3, or $(BiO)_2CO_3$ in nitric acid. Attempts to remove the water of hydration yield monoclinic crystals of bismuthyl nitrate hemihydrate, $BiONO_3{\cdot}1/2H_2O$ [10361-64-3] (41). Addition of bismuth trinitrate pentahydrate to alkali yields a product termed bismuth subnitrate that is widely used in pharmaceuticals. This material approximates the composition $6Bi_2O_3{\cdot}5N_2O_5{\cdot}9H_2O$.

Bismuth Trisulfate. Bismuth(III) sulfate, $Bi_2(SO_4)_3$ [7787-68-0], is a colorless, very hygroscopic compound that decomposes >405°C to yield bismuthyl salts and Bi_2O_3. The compound hydrolyzes slowly in cold water and rapidly in hot water to the yellow bismuthyl sulfate, $(BiO)_2SO_4$ [12010-64-9]. The normal sulfate is isomorphous with the sulfates of yttrium, lanthanum, and praseodymium.

Numerous other bismuth and bismuthyl salts are known, eg, bismuth triacetate, $Bi(C_2H_3O_2)_3$ [22306-37-2]; bismuth phosphate, $BiPO_4$ [10049-01-1]; bismuth trithiocyanate, $Bi(SCN)_3$ [43384-63-0]; bismuthyl nitrite hemihydrate, $BiO(NO_2){\cdot}1/2H_2O$ [66172-94-9]; bismuthyl carbonate hemihydrate, $(BiO)_2 CO_3{\cdot}1/2H_2O$ [5798-45-8]; etc. Bismuth is present in the anion in the oxalato complex sodium dioxalatobismuthate(III), $NaBi(C_2O_4)_2$ [19033-91-1], the nitrito complex trisodium hexanitrobismuthate(III), $Na_3Bi(NO_2)_6$ [18515-86-1], and the yellow, water-soluble thiosulfato complex trisodium trithiosulfatobismuthate(III), $Na_3Bi(S_2O_3)_3$ [66256-75-5].

3.9. Alkoxides, Thiolates, Carboxylates, and Related Compounds. Alkoxides of bismuth, $Bi(OR)_3$ (R = alkyl, aryl) are potential precursors for bismuth-containing superconductors. They are obtained by reaction of $BiCl_3$ with NaOR or by other methods (42). Depending on the size of the R group the alkoxides are monomeric or polymeric (43,44). A thiolate with a known crystal structure is $Bi(SR)_3$ ($R = 2,4,6\text{-}[(CH_3)_3C]_3C_6H_2$) (45). Complexes of Bi(III) with the SCH_2CH_2OH ligand have been studied with respect to structural aspects and to the antimicrobial potential of these compounds (46,47). Recently studied carboxylates of Bi(III) include mono or bidentate complexes with the ligands CH_3COO (48), $CH_3CH(OH)COO$ (49), $(CH_3)_3COO$ (50), CF_3COO (51). Also complexes with bidentate thio ligands, eg, $S_2P(C_6H_5)_2$ (52), or $S_2COC_2H_5$ (53) are known.

3.10. Compounds with Bismuth Metal Bonds. Bonds between Bi and transition metals including Cr, Mo, W, Mn, Fe, Co, Ru, Ir, Os, Ni exist in clusters. The structures and chemistry of these compounds have been reviewed recently (54). Also compounds with bonds between Bi main group metals or semimetals, eg, Ge (55) or Si (56) are known.

4. Organobismuth Compounds

In a manner similar to phosphorus, arsenic, and antimony, the bismuth atom can be either tri- or pentacovalent. However, organobismuth compounds are less stable thermally than the corresponding phosphorus, arsenic, or antimony compounds, and there are fewer types of organobismuth compounds. For example, with R_4MX, R_3MX_2, R_2MX_3, and RMX_4, where M is a Group 15 (VA) element and X is a halogen, only the first two types have been prepared where $M = Bi$, but all four types are known where $M = P$, As, or Sb. The chemistry of organobismuth compounds has been described in several publications (26,57-63). The use of organobismuth compounds, as well as organoantimony ones, in organic synthesis has been exhaustively reviewed (64).

4.1. Primary and Secondary Bismuthines. Unstable methylbismuthine, CH_3BiH_2, and dimethylbismuthine, $(CH_3)_2BiH$ (6) are prepared by the lithium aluminum hydride reduction of methyldichlorobismuthine, CH_3BiCl_2 [105309-90-8] and dimethylchlorobismuthine, respectively, in a nitrogen atmosphere at $-150°C$. On being warmed to $-45°C$, methylbismuthine disproportionates to trimethylbismuthine, $(CH_3)_3Bi$ [593-91-9], and bismuthine. Dimethylbismuthine undergoes a similar disproportionation at $-15°C$. Both methyl- and dimethylbismuthine are stable, colorless liquids at $-60°C$, but at room temperature they decompose to trimethylbismuthine, bismuth, and hydrogen. An attempt to prepare phenylbismuthine and diphenylbismuthine, $(C_6H_5)_2BiH$ [14381-43-2] by reduction of phenyldibromobismuthine, $(C_6H_5)_2$ BiBr [39110-02-6] and diphenylbromobismuthine, $(C_6H_5)_2BiBr$, [39248-62-9], respectively, with $LiAlH_4$ or sodium borohydride at low temperatures yielded only black polymeric substances of empirical formula C_6H_5Bi (65). A stable organobismuth hydride, $(2,6\text{-}Mes_2C_6H_3)_2BiH$ ($Mes = 2,4,6\text{-}(CH_3)_3C_6H_2$) (66) is obtained by reduction of the corresponding chloride with $LiAlH_4$. The signal for ν Bi–H appears at $1759\ cm^{-1}$ in the ir spectrum. $(2,6\text{-}Mes_2C_6H_3)_2BiH$ decomposes at 135 °C with formation of the dibismuthene, $(2,6\text{-}Mes_2C_6H_3Bi)_2$ (66).

4.2. Tertiary Bismuthines. A large number of trialkyl- and triarylbismuthines are known (58). They are usually prepared by the interaction of a reactive organometallic compound and a bismuth trihalide, a halobismuthine, or a dihalobismuthine. The Grignard reagent (see GRIGNARD REAGENTS) is the type of organometallic compound most widely employed in these syntheses (67–69). Organolithium (70-72), and other organometallic compounds (73–79) have also been used. Triphenylbismuthine, $C_{18}H_{15}Bi$ [603-33-8], has been obtained in a 50% yield by the addition of phenyltrifluorosilane and ammonium fluoride to a solution of bismuth hydroxide in hydrofluoric acid (80). The interaction of organomercury compounds and metallic bismuth has also been employed for the preparation of tertiary bismuthines (81).

A number of unsymmetrical tertiary bismuthines have been prepared by the interaction of a sodium diaryl- or dialkylbismuthide and an alkyl or aryl halide (82). There have been several reports of the formation of tertiary bismuthines by the action of free radicals on metallic bismuth. One method of generating the radicals involves cleavage of ethane or hexafluoroethane in a radiofrequency glow discharge apparatus; the radicals thus formed are allowed to oxidize the metal at −196°C (83). Trimethylbismuthine and tris(trifluoromethyl)bismuthine, $(CF_3)_3Bi$ [5863-80-9] have been obtained by this procedure.

Trialkylbismuthines are colorless or pale yellow liquids or solids, and most of them are spontaneously flammable in air. Except for trimethylbismuthine, these compounds cannot be distilled at ordinary pressures without decomposition (84). In general, trialkylbismuthines are not affected by water or aqueous bases but are readily hydrolyzed by many inorganic and organic acids (85,86). Trialkylbismuthines generally react with chlorine and bromine at low temperatures to form dialkylhalobismuthines (77,78). The reaction of tris(trifluoromethyl)bismuthine with chlorine, bromine, or iodine, however, has been found to yield the corresponding bismuth trihalide and trifluoromethyl halide (87). Triarylbismuthines are solids, which usually have sharp melting points. Most of these compounds are unaffected by oxygen or water at ordinary temperature and are, in general, much less reactive than their trialkyl counterparts. Triphenylbismuthine can be readily distilled, bp 242°C at 1.9 kPa without decomposition, and it has been obtained so pure that it has been used in measurements of the atomic weight of bismuth (88).

Most triarylbismuthines readily undergo oxidative addition with bromine or chlorine to yield the corresponding triarylbismuth dihalides:

$$Ar_3Bi + X_2 \longrightarrow Ar_3BiX_2 \qquad (2)$$

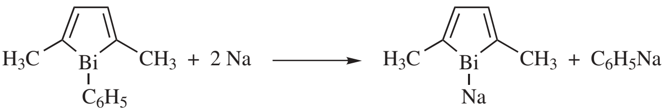
Triphenylbismuth difluoride, $(C_6H_5)_3BiF_2$ [2023-48-5] has been obtained in a similar manner (89). All three carbon–bismuth bonds of tribenzylbismuthine, $C_6H_5CH_2)_3Bi$ [99715-52-3] (90) and triphenylbismuthine (91) can be cleaved by alkali metals. Under some conditions, however, tertiary bismuthines react with sodium or potassium to yield secondary bismuthides. Thus a number of sodium dialkylbismuthides have been obtained by the interaction of a trialkylbismuthine and sodium in liquid ammonia (92–95):

$$R_3Bi + 2\ Na \longrightarrow R_2BiNa + RNa \qquad (3)$$

where $R = CH_3$, C_2H_5, n-C_3H_7, iso-C_3H_7, or n-C_4H_9. Triphenylbismuthine reacts with potassium in tetrahydrofuran (thf) in a similar manner (96):

$$(C_6H_5)_3Bi + 2\ K \longrightarrow (C_6H_5)_2BiK + C_6H_5K \qquad (4)$$

Treatment of 1-phenyl-2,5-dimethylbismole, $C_{12}H_{13}Bi$ [88635-81-8], with sodium in liquid ammonia results in cleavage of the phenyl–bismuth bond and formation of 1-sodio-2,5-dimethylbismole, C_6H_8BiNa [88644-52-4] (97):



(5)

The secondary bismuthides discussed herein are useful for preparing several types of organobismuth compounds, eg, tertiary bismuthines and dibismuthines. Reaction of diphenylmethyl bismuthine with gaseous HCl or HBr results in the substitution of the phenyl groups by halogen atoms (98).

Although trialkyl- and triarylbismuthines are much weaker donors than the corresponding phosphorus, arsenic, and antimony compounds, they have nevertheless been employed to a considerable extent as ligands in transition metal complexes. The metals coordinated to the bismuth in these complexes include chromium (99–104), cobalt (105,106), iridium (107), iron (104,108,109), manganese (110,111), molybdenum (99,102–108,112–116), nickel (102,106,117, 118), niobium (119), rhodium (120,121), silver (122–124), tungsten (99,102–104,114,115), uranium (125), and vanadium (126). The coordination compounds formed from tertiary bismuthines are less stable than those formed from tertiary phosphines, arsines, or stibines. Several types of compounds containing an organometallic R_nBi ($n = 1$ or 2) moiety attached to a transition metal atom are also known (26). Examples are $Ph_2BiMn(CO)_5$, $MeBi(Fe(CO)_4)_2$ (127), or the cluster $[W_2(CO)_8(\mu\text{-}\eta^2\text{-}Bi_2)\text{-}\mu\text{-}MeBiW(CO)_5]\cdot C_6H_6$ (128).

Tertiary bismuthines appear to have a number of uses in synthetic organic chemistry (64), eg, they promote the formation of 1,1,2-trisubstituted cyclopropanes by the interaction of electron-deficient olefins and dialkyl dibromomalonates (129). They have also been employed for the preparation of thin films (qv) of superconducting bismuth strontium calcium copper oxide (130), as cocatalysts for the polymerization of alkynes (131), as inhibitors of the flammability of epoxy resins (132), and for a number of other industrial purposes.

4.3. Halobismuthines, Dihalobismuthines, and Related Compounds. Chloro-, dichloro-, bromo-, and dibromobismuthines are prepared by the reaction of a tertiary bismuthine and bismuth trichloride or tribromide (6,75,77,78,133–137):

$$R_3Bi + 2\,BiX_3 \longrightarrow 3\,RBiX_2 \tag{6}$$

$$2\,R_3Bi + BiX_3 \longrightarrow 3\,R_2BiX \tag{7}$$

Pure samples of CH_3BiCl_2 or CH_3BiBr_2 were obtained by reaction of CH_3BiPh_2 with HCl or HBr (98). Iodo- and diiodobismuthines are easily obtained by the reaction of the corresponding chloro-, dichloro-, bromo-, or dibromobismuthine with sodium or potassium iodide (137–140). Several halo- and dihalobismuthines have been prepared by the partial alkylation or arylation of bismuth trichloride or tribromide with an organocadmium (141), organolead (142,143), organotin (144,145), or organozinc reagent (77). The reaction of a Grignard reagent with a bismuth trihalide usually leads to the formation of a tertiary bismuthine. In a few cases, however, it has been possible to isolate a halo or dihalobismuthine from this type of reaction (146). The reaction of RLi [$R = (Me_3Si)_2CH$] with $BiCl_3$ in the 2:1 molar ratio gives R_2BiCl (147). $RBiCl_2$ [$R = (Me_3Si)_2CH$] is obtained from $RBiPh_2$ and HCl (147). Apparently, no fluoro- or difluorobismuthine has ever been isolated. The formation of bis(trifluoromethyl)fluorobismuthine [124252-79-5] by the interaction of tris(trifluoromethyl)bismuthine and iodine pentafluoride has, however, been suggested by ^{19}F nmr spectroscopy (148).

Halo- and dihalobismuthines are crystalline solids, many of which have polymeric structures (26) with melting points >100°C. They are, in general, decomposed by moisture, alcohols, and ammonia (149). Dialkylhalobismuthines are especially sensitive substances. The diaryl compounds are more stable, but they should also be handled with caution. Some of them are powerful sternutators (150).

Diphenylhalobismuthines and phenyldihalobismuthines react with tetraorgano ammonium, phosphonium, or arsonium salts to give compounds of the type $[R_4E][Ph_2BiX_4]$ or $[R_4E][PhBiX_3]$ where the bismuth moiety is anionic (151–153).

A number of compounds of the types $RBiY_2$ or R_2BiY, where Y is an anionic group other than halogen, have been prepared by the reaction of a dihalo- or halobismuthine with a lithium, sodium, potassium, ammonium, silver, or lead alkoxide (154,155), amide (156,157), azide (158,159), carboxylate (155,160), cyanide (159,161), dithiocarbamate (162,163), dithiophosphinate (133), mercaptide (164,165), nitrate (138), phenoxide (154), selenocyanate (159), silanolate (166), thiocyanate (159), or xanthate (167). Dialkyl- and diarylhalobismuthines can also be readily converted to secondary bismuthides by treatment with an alkali metal (82,135,168):

$$R_2BiX + 2\,M \longrightarrow R_2BiM + MX \qquad (8)$$

4.4. Ionic and Neutral Organobismuth Complexes with π-Bonding or Hypervalency. Cyclopentadienyl bismuth dihalides and related compounds (26,169,170,171) belong to the group of compounds with π-bonding between the metal and the organic ligands. With two substituted cyclopentadienyl ligands coordinated on bismuth the formation of a bismocenium salt, $Cp^x{}_2Bi^+AlCl_4^-$ ($Cp^x = 1,2,4\text{-}t\text{-}Bu_3C_5H_2$) is achieved (171). Other known cations derived from organobismuth halides are $R_2BiL_2^+$ and $RBiL_4^+$ [$R = Ph$, $L = (Me_2N)_3PO$] (172). A cationic hypervalent complex stabilized through intermolecular coordination is $[2\text{-}(Me_2NCH_2)C_6H_4]_2Bi^+$, where both nitrogen atoms are strongly coordinated to the bismuth center (173). Also, neutral hypervalent complexes with intramolecular coordination are known. Examples are $2\text{-}(Me_2NCH_2)C_6H_4BiC_6H_4\{C(CF_3)_2O\}\text{-}2$ and related compounds (174).

4.5. Dibismuthines, Dibismuthenes, and Cyclo-Bismuthines About a dozen dibismuthines are known (175). These compounds can be obtained by the reaction of a sodium dialkyl- or diarylbismuthide and a 1,2-dihaloethane (92–95):

$$2\,R_2BiNa + XCH_2CH_2X \longrightarrow R_2BiBiR_2 + H_2C{=}CH_2 + 2\,NaX \qquad (9)$$

where X = Cl or Br. Several dibismuthines have also been obtained by the addition of the stoichiometric amount of sodium to a solution of a halobismuthine in liquid ammonia (135,176–179):

$$2\,R_2BiX + 2\,Na \longrightarrow R_2BiBiR_2 + 2\,NaX \qquad (10)$$

where X = Cl or I. The best method for the synthesis of tetraphenyldibismuthine, $(C_6H_5)_4Bi_2$ [7065-21-6] involves the reduction of diphenyliodobismuthine,

$(C_6H_5)_2BiI$ [95825-92-6] using bis(cyclopentadienyl)cobalt(II), $(C_5H_5)_2Co$ [1277-43-6], (180):

$$2\,(C_6H_5)_2BiI + 2\,Co(C_5H_5)_2 \longrightarrow (C_6H_5)_2BiBi(C_6H_5)_2 + 2\,(C_5H_5)_2CoI \qquad (11)$$

Dibismuthines tend to be thermally unstable. Thus tetramethyldibismuthine, $C_4H_{12}Bi_2$ [82783-70-8] decomposes at 25°C to yield trimethylbismuthine and metallic bismuth (92):

$$3\,(CH_3)_2BiBi(CH_3)_2 \longrightarrow 4\,(CH_3)_3Bi + 2\,Bi \qquad (12)$$

Tetraethyldibismuthine, $C_8H_{20}Bi_2$, [81956-27-6], undergoes a similar reaction at 40°C (93). At 0°C this dibismuthine as well as tetra-4-tolyldibismuthine, $C_{28}H_{28}Bi_2$ [114245-28-2] (135) decompose to form dark polymeric solids:

$$R_2BiBiR_2 \longrightarrow R_3Bi + 1/x(RBi)_x \qquad (13)$$

where $R = C_2H_5$ or $4\text{-}CH_3C_6H_4$. Tetraphenyldibismuthine and 2,2′,5,5′-tetramethylbibismole, $C_{12}H_{16}Bi_2$ [88635-82-9] (97), however, are stable to 100°C.

Dibismuthines are very sensitive to oxidation. Thus tetramethyldibismuthine fumes in air, and tetraphenyldibismuthine in toluene solution rapidly absorbs oxygen. Under controlled conditions, dibismuthines react with chalcogens resulting in cleavage of the bismuth–bismuth bond and insertion of a chalcogen atom (135,178,180–182):

$$R_2BiBiR_2 + Y \longrightarrow R_2BiYBiR_2 \qquad (14)$$

where Y = O, S, Se, or Te. Dibismuthines undergo a variety of other interesting reactions and have attracted considerable attention because a number of these substances are thermochromic (175,183).

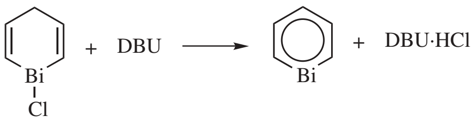
Only two cyclobismuthines, a trimer $(RBi)_3$ and a tetramer $(RBi)_4$ have been reported in the literature. In benzene solution, the two rings exist in an equilibrium. On crystallization, the equilibrium is shifted to the tetramer (184,185).

Dibismuthenes, RBi=BiR, involving double bonds between the bismuth centers, exist as stable compounds with bulky aryl substituents ($R = 2,4,6\text{-}[(Me_3Si)_2CH]_3C_6H_2$, (Tbt); $2,6\text{-}[(Me_3Si)_2CH]_2\text{-}4\text{-}(Me_3Si)_3C\text{-}C_6H_2$, (Bbt); $R = 2,6\text{-}Mes_2C_6H_3$, $2,6\text{-}Trip_2C_6H_3$ ($Trip = 2,4,6\text{-}i\text{-}Pr_3\text{-}C_6H_2$); $Me = CH_3$, $i\text{-}Pr = (CH_3)_2CH$. RBi=BiR (R = Tbt) was formed by deselenation of $(RBiSe)_3$ (R = Tbt) with $(Me_2N)_3P$ (186–188). Dehalogenation of $RBiBr_2$ with Mg in thf gave RBi=BiR (R = Bbt) (188). The terphenyl substituted dibismuthenes, RBi=BiR ($R = 2,6\text{-}Mes_2C_6H_3$, $2,6\text{-}Trip_2C_6H_3$); $Mes = 2,4,6\text{-}(CH_3)_3C_6H_2$ are synthesized by reduction of the corresponding aryl bismuth dichlorides with potassium in toluene/hexane (189,190) or by decomposition of R_2BiH ($R = 2,6\text{-}Mes_2C_6H_3$) (66). The dibismuthenes are purple solids soluble without dissociation in organic solvents. Attempts to trap RBi momomers with dienes failed. The length of the Bi–Bi double bond in RBi=BiR [R = Tbt, 2.8206 (8) Å] is 6 % shorter than the Bi–Bi single bond length of $Ph_2Bi\text{–}BiPh_2$ [2.990(2)Å] (178). The condensation reaction of $RSbH_2$ with $RBiBr_2$ (R = Bbt) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene

(DBU) in thf afforded a stibabismuthene RSb=BiR (R = Bbt) (191), which in benzene at 70°C reacts to RSb=SbR and RBi=BiR (R = Bbt). This reaction does not involve the formation of RBi or RSb units, instead the formation of a bismuth antimony ring compound as intermediate is assumed.

Thermolysis of bismuth trifluoracetate in presence of Me_6C_6 gives $[Bi_2(O_2CCF_3)_4]\cdot C_6Me_6$. Crystals of this compound consist of stacks o trifluoroacetato bridged dibismuth units with Bi–Bi bond lengths of 2.947(1) Å and η^6-coordinated Me_6C_6 units in bridging positions (192).

4.6. Bismin and Its Derivatives. Bismin (bismabenzene), C_5H_5Bi [289-52-1], the bismuth analogue of pyridine, has never been isolated, but it can be formed in solution by the dehydrohalogenation of 1-chloro-1,4-dihydrobismin, C_5H_6BiCl [39553-69-0], using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at low temperatures (144,193,194):



(15)

4-Methylbismin, $CH_3C_5H_4Bi$ [82995-62-8] and 4-tert-butylbismin, $(CH_3)_3CC_5H_4Bi$ [82995-64-0], have been obtained in solution by similar reactions. The presence of bismin and its 4-alkyl derivatives in these solutions has been demonstrated both by spectroscopy and via chemical trapping with 1,1,1,4,4,4-hexafluoro-2-butyne to yield Diels–Alder adducts. The potential aromaticity of the bismin ring system has aroused considerable interest and has been investigated with a variety of spectral methods. There seems to be little doubt that bismin does possess aromatic character.

4.7. Diarylbismuthinic Acids and Their Esters. A number of methyl diarylbismuthinates (diarylmethoxybismuth oxides) $Ar_2Bi(O)OCH_3$ (Ar = C_6H_5, 4-$CH_3C_6H_4$, 3,4-$(CH_3)_2C_6H_3$, 1-naphthyl, or 4-CH_3-1-naphthyl) were reported in 1988 (195). The methyl esters underwent ester exchange when recrystallized from ethyl or isopropyl alcohols. Methyl diphenylbismuthinate, $C_{13}H_{13}BiO_2$ [124066-62-2], was readily hydrolyzed in water to diphenylbismuthinic acid [124066-70-2]. Because organobismuth(V) compounds have found considerable use as oxidizing agents, the oxidizing ability of methyl di-1-naphthylbismuthinate, $C_{21}H_{17}BiO_2$ [124066-66-6] was investigated. Benzoin yields benzil, naphthalene, and metallic bismuth; hydrazobenzene yields azobenzene, and 1,1,2,2-tetraphenylethanediol yields benzophenone. 1,2-Diphenyl-1,2-ethanedione dihydrazone gives diphenylacetylene in 50% yield. Cyclohexane-1,2-diol and 1-phenylethane-1,2-diol, however, were unaffected (62,195,196).

4.8. Trialkyl- and Triarylbismuth Dihalides and Related Compounds. The triarylbismuth dihalides constitute an important class of organobismuth compounds. Only very few trialkylbismuth dihalides are kown. Trimethylbismuth dichloride, prepared by oxidative chlorination of Me_3Bi with SO_2Cl_2 at −78°C is unstable at room temperature. The geometry of the C_3BiCl_2 core in crystals of $Me_3BiCl_2\cdot Me_2CO$ is distorted trigonal bipyramidal (197). The formation of the cis and trans-isomers of tripropenylbismuth dibromide, $C_9H_{15}BiBr_2$, [66173-00-0, 66212-22-4] by oxidative bromination of the corresponding bismuthines at $-55°C$ was reported in 1963 (198). With other trialkylbismuthines studied, cleavage of one carbon−bismuth bond occurs on halogenation:

$$R_3Bi + X_2 \longrightarrow R_2BiX + RX \tag{16}$$

By contrast, triarylbismuthines are readily chlorinated or brominated to the corresponding dichlorides or dibromides using chlorine or bromine. Other chlorinating agents include sulfur dichloride, sulfur monochloride, thionyl chloride, and iodine trichloride. Triarylbismuth difluorides have been prepared from the dichlorides by metathesis with potassium fluoride or by direct fluorination of triarylbismuthines with fluorine diluted with argon. No triarylbismuth diiodides are known. However, the two compounds triphenylbismuth iodide azide, $(C_6H_5)_3Bi(I)N_3$, [106112-77-0] and triphenylbismuth iodide isocyanate, $(C_6H_5)_3BI(I)NCO$ [106112-78-1], have been prepared from triphenylbismuthine and iodine azide or iodine isocyanate, respectively (199). The triarylbismuth dihalides are stable crystalline solids with high melting points. X-ray studies, conductivities, and other physical measurements suggest that the bismuth atom in these compounds has trigonal−bipyramidal geometry (26).

In addition to the halides Ar_3BiX_2, a large number of compounds of the type Ar_3BiY_2, where Y is NO_3, N_3, CN, OCN, CH_3CO_2, CF_3CO_2, ½ CO_3, ½ SO_4, O_3SR, etc, can be prepared by metathesis from the dihalides and a silver, sodium, or potassium salt of the desired anion. The disulfonates $(C_6H_5)_3Bi(O_3SR)_2$ have been prepared from the carbonate and the appropriate sulfonic acid (200). A number of mixed carbonates $Ar_2Ar'BiCO_3$, as well as mixed dichlorides $Ar_2Ar'BiCl_2$, have been prepared (201). Triphenylbismuth dicarboxylates have been obtained by several different methods including the following (202):

$$(C_6H_5)_3Bi + (CH_3)_3COOH + (RCO)_2O \longrightarrow (C_6H_5)_3Bi(O_2CR)_2 + (CH_3)_3COH \tag{17}$$

The majority of the compounds of the type Ar_3BiY_2 are stable crystalline solids, soluble in organic solvents. They give normal molecular weights in solvents such as benzene and have more or less distorted trigonal bipyramidal structures (26).

Triphenylbismuth oxide, $C_{18}H_{15}BiO$ [7173-99-1] has been prepared from triphenylbismuth dicyanide, $C_{20}H_{15}BiN_2$ [41083-16-3] and mercuric oxide (203), and from triphenylbismuth dichloride and moist silver oxide (204). The ir and Raman spectra of this compound suggest that it is polymeric and has Bi−O−Bi bonds (205). Triphenylbismuth dihydroxide and triarylbismuth hydroxide halides, eg, triphenylbismuth hydroxide chloride have been reported in the earlier chemical literature (206). There is, however, no modern research on these types of compounds, and they may or may not exist.

In recent years organobismuth(V) compounds have found increasing use as reagents in organic synthesis. Thus they have been used for the oxidation of primary and secondary alcohols to the corresponding aldehydes (qv) and ketones (qv), for the oxidative cleavage of vicinal glycols (qv), and for the O-, C-, and N-arylation of a wide variety of organic compounds. Because most of these reactions occur under relatively mild conditions, organobismuth(V) reagents have proved to be of particular value when the substrates are sensitive natural products. Several review articles on this subject have been published (64,207–209), and a patent on the oxidation of steroids, terpene, and sugar alcohols to the corresponding aldehydes (qv) and ketones (qv) has been issued (210) (see SUGAR ALCOHOLS). Although other types of organobismuth(V) compounds, Ar_4BiY and Ar_5Bi, have been used, the triaryl compounds Ar_3BiY_2 are the reagents of choice because of their ease of preparation and chemical stability.

In addition to use in organic synthesis, triarylbismuth dihalides and related compounds have found limited industrial use. A patent has been issued for the use of such compounds as antifungal agents on plastics or fibrous material (211). Compounds of the type $(C_6H_5)_3Bi(O_2CR)_2$, eg, triphenylbismuth dimethacrylate, $C_{26}H_{25}BiO_4$ [3371-98-0] and triphenylbismuth bis(4-vinylbenzoate), $C_{36}H_{29}BiO_4$ [2181-48-8] are claimed to be effective agents against *Staphylococcus aureus* infections (212). Triphenylbismuth dichloride, $(C_6H_5)_3BiCl_2$ [594-30-9] is active against bean rust (213). Triarylbismuth dihalides have been used as catalysts for the carbonation of epoxides to form cyclic carbonates (214).

4.9. Quaternary Bismuth Compounds. Although earlier attempts had been made to prepare quaternary bismuth compounds, it was not until 1952 that tetraphenylbismuth bromide, $(C_6H_5)_4BiBr$ [66173-02-2] was obtained from pentaphenylbismuth, $(C_6H_5)_5Bi$ [3049-07-8] and 1 M equivalent of bromine at −70°C (215):

$$(C_6H_5)_5Bi + Br_2 \longrightarrow (C_6H_5)_4BiBr + C_6H_5Br \qquad (18)$$

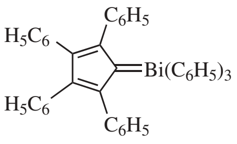
In a similar manner, tetraphenylbismuth chloride, $(C_6H_5)_4BiCl$ [42967-53-3] (215) and tetraphenylbismuthonium tetrafluoroborate, $(C_6H_5)_4Bi[BF_4]$ [36682-02-7] (216) are obtained from pentaphenylbismuth and hydrogen chloride or hydrogen tetrafluoroborate, respectively. When triphenylboron is used, the tetraphenylborate is obtained (215):

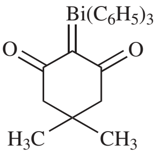
$$(C_6H_5)_5Bi + (C_6H_5)_3B \longrightarrow \left[(C_6H_5)_4Bi\right]\left[(C_6H_5)_4B\right] \qquad (19)$$

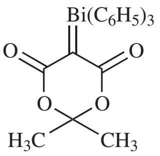
A number of other tetraarylbismuth compounds Ar_4BiY, where Y is a group, such as NO_3^-, ClO_4^-, OCN^-, N_3^-, etc, have been prepared from the chloride by metathesis. Tetramethylbismuthonium trifluoromethylsulfonate, a crystalline compound stable at 150°C is formed from $(CH_3)_3Bi$ and $CH_3OSO_2CF_3$ (198). Also the formation of $[CH_3(C_2H_5)_3Bi][BF_4]$ (217) and $[(C_6H_5)_3BiCH_2COCH_3][ClO_4]$ (218) was reported. When triphenylbismuth dichloride, in acetone, is treated with silver perchlorate, in absolute ethanol, tetraphenylbismuthonium perchlorate, $(C_6H_5)_4BiClO_4$ [43047-28-5] is formed (219). Many quaternary bismuth compounds are unstable. When the anionic ligand is chloride or bromide, the compounds decompose spontaneously on standing; azides and selenocyanates decompose more rapidly. The perchlorates, tetrafluoroborates, and hexafluorophophates, however, are considerably more stable but eventually decompose. Quaternary bismuth compounds have not found extensive use in industry or in organic synthesis. In manifold studies of organobismuth(V) compounds as oxidizing and arylating agents, such quaternary bismuth compounds as $(C_6H_5)_4BiO_2CCH_3$, $(C_6H_5)_4BiO_3SC_6H_4CH_3$-4, and $(C_6H_5)_4BiO_2CCF_3$ have been employed (64).

There seems to be no marked advantage of the quaternary compounds over the more stable and more easily prepared compounds of the type Ar_3BiY_2.

4.10. Bismuthonium Ylides. Prior to 1988 the only bismuthonium ylides known were (1) and (2).

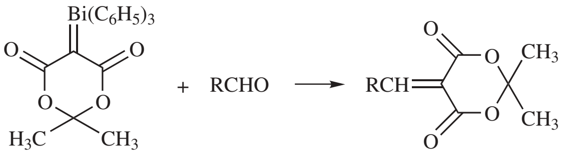

(1)


(2)

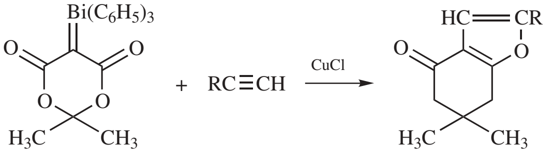

(3)

Compound (1) is an unstable blue solid that cannot be obtained in a pure state (220); structure (2) [105071-90-7], however, is stable (221). Compound (2) was obtained from triphenylbismuth carbonate and dimedone. More recently a number of bismuthonium ylides, eg, (3) [119016-81-8] (222), have been prepared and their reactions studied.

Reactions of these compounds with phenylisothiocyanate and a number of aromatic and aliphatic aldehydes have been investigated (222,223). Only where R is $4\text{-}CH_3OC_6H_4$ or $C_6H_5CH{=}CH$ are the normal Wittig products obtained:


(20)

By using a number of other aldehydes, more complicated products result. Structure (2) was also found to react with alkynes in the presence of copper(I) chloride to give furans:

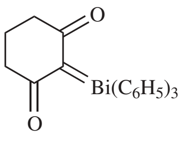

(21)

where R is C_6H_5, $4\text{-}CH_3C_6H_4$, $4\text{-}ClC_6H_5$, hexyl, and $C_6H_5COCH_2$. An excellent general method for the preparation of bismuthonium ylides from diazo compounds has been devised in which bis(hexafluoroacetylacetonato)copper(II) is employed as a catalyst (224). Two relatively stable ylides prepared by this procedure are (4) [117968-30-6] and (5) [117968-31-7]. The latter compound did not react with 2,4-dinitrobenzaldehyde.

$$(C_6H_5SO_2)_2C{=}Bi(C_6H_5)_3 \qquad (4)$$

$(C_6H_5SO_2)_2C{=}Bi(C_6H_5)_3$

(4)


(5)

4.11. Qinquenary Bismuth Compounds.

A number of pentaarylbismuth compounds and pentamethylbismuth are known. Pentaphenylbismuth, $C_{30}H_{25}Bi$ [3049-07-8] was first prepared by means of the following reaction (215):

$$(C_6H_5)_3BiCl_2 + 2\ C_6H_5Li \longrightarrow (C_6H_5)_5Bi + 2\ LiCl \tag{22}$$

It can also be prepared by the reaction of phenyllithium with tetraphenylbismuth chloride or the *N*-triphenylbismuth derivative of 4-toluenesulfonamide (225):

$$\begin{aligned}4 - CH_3C_6H_4SO_2N{=}Bi(C_6H_5)_3 + 2C_6H_5Li \longrightarrow& \\ (C_6H_5)_5Bi + 4 - CH_3C_6H_4SO_2NLi_2&\end{aligned} \tag{23}$$

Pentaphenylbismuth is a violet-colored, crystalline compound that decomposes spontaneously after standing for several days in a dry nitrogen atmosphere. With a variety of agents, eg, hydrohalic acids, halogens, and triphenylboron, one phenyl group is cleaved to form quaternary bismuth compounds (62). The deep violet color of pentaphenylbismuth and certain other pentaarylbismuth compounds has been the subject of considerable speculation. It has been shown by X-ray diffraction (226) that the bismuth atom in pentaphenylbismuth is square–pyramidal. Well-formed crystals are dichromic, appearing violet when viewed in one plane but colorless in another plane. The nature of the chromophore has been suggested to be a charge-transfer transition by excitation of the four long equatorial bonds:

$$(C_6H_5)_4Bi - C_6H_5 \longrightarrow (C_6H_5)_4Bi^{-}C_6H_5^{+} \tag{24}$$

In support of this suggestion, it has been shown that strong electron-withdrawing substituents on the aryl groups, which would make the charge-transfer transition more difficult, result in less highly colored compounds. Thus bis(pentafluorophenyl)triphenylbismuth, $C_{30}H_{15}BiF_{10}$ [111210-36-7] is an orange-colored solid. A number of pentaarylbismuth compounds that vary in color from violet, bis(4-fluorophenyl)tri-4-tolylbismuth, $C_{33}H_{29}BiF_2$ [124652-38-6] to yellow, bis(pentafluorophenyl)tri-4-tolylbismuth, $C_{33}H_{21}BiF_{10}$ [118798-77-9] have been prepared (227). The majority of structures that could be determined by x-ray diffraction exhibit square pyramidal geometry. Pentamethylbismuth, a violet crystalline compound, decomposing with explosion at room temperature is obtained by reaction of Me_3BiCl_2 with MeLi at $-95°C$ (198). The crystal structure of Me_5Bi is trigonal bipyramidal (198).

Pentaphenylbismuth has been studied as a reagent in organic synthesis where it can act either as an oxidizing or an arylating agent. Thus it can be used for the oxidation of primary or secondary alcohols to aldehydes or ketones, respectively. Unlike compounds of the type Ar_3BiY_2 or Ar_4BiY that require the presence of a strong base for the oxidation of alcohols, pentaphenylbismuth oxidizes alcohols under neutral conditions. Thus benzyl alcohol is oxidized to benzaldehyde in 45% yield by pentaphenylbismuth; 3β-cholestanol gives the corresponding ketone in 70% yield. Pentaphenylbismuth can also act as an arylating agent. 2-Naphthol reacts to give 1-phenyl-2-naphthol in 61% yield

(C-arylation), but phenol gives diphenyl ether in 42% yield (O-arylation). Often both oxidation and phenylation occur. Thus estradiol gives a mixture of 2,4-diphenylestrone, 4-phenylestrone, and 2,4-diphenylestradiol. When 2-phenylethanol is treated with pentaphenylbismuth, triphenylacetaldehyde is produced in 69% yield (62,209).

5. Bismuth Compounds Used in Medicine

Therapeutic properties were first attributed to bismuth during the seventeenth century, and bismuth compounds were tried for the treatment of both syphilis and gonorrhea before the end of the eighteenth century (149). During the 1920s, it was shown that bismuth compounds were comparable in efficacy to the best antisyphilic drugs then available (228). During the next quarter of a century, bismuth compounds became widely used as adjuncts to the arsenical therapy of syphilis (229). However, antibiotics (qv), especially penicillin, have made both arsenic and bismuth compounds completely obsolete for the treatment of this disease (230,231). Bismuth compounds were employed for the treatment of amoebic dysentery, certain skin diseases, and several spirochetal diseases besides syphilis, but these substances are now seldom considered the drugs of choice. Various insoluble preparations of bismuth, especially the subcarbonate, subnitrate, subgallate, subcitrate, and subsalicylate, are employed for the treatment of gastrointestinal disorders. By the time *H. pyloris* was recognized as being central for the formation of ulcers in the stomach the use of bismuth preparations was appreciated. Eradication of *H. pyloris* is achieved by means of a combination therapy that uses bismuth compounds and other substances. Reviews of the biological activity of organobismuth compounds have been published (232–236). Bismuth subsalicylate, [14882-18-9], Pepto-Bismol, is a basic salt of varying composition, corresponding approximately to o-$HOC_6H_4CO_2(BiO)$. It does appear to be effective for the relief of mild diarrhea and for the prevention of travelers' diarrhea (233) in the symptomatic treatment of isosporiasis, a disease caused by the intracellular parasite *Isospora belli* (237). Bismuth subcarbonate (basic bismuth carbonate) [5892-10-4] is a white or pale yellow powder that is prepared by interaction of bismuth nitrate and a water-soluble carbonate. The exact composition of this drug depends on the conditions of precipitation; it corresponds approximately to the formula $(BiO)_2CO_3$. It has been widely used as an antacid (238). Tripotassium dicitratobismuthate, (bismuth subcitrate), [57644-54-9], De-Nol is a buffered aqueous suspension of a poorly defined, water-insoluble bismuth compound. It is said to be very effective for the treatment of gastric and duodenal ulcers (233,238). There have not yet been any reports of bismuth encephalopathy following the use of this drug. Bismuth subnitrate (basic bismuth nitrate), [1304-85-4] can be prepared by the partial hydrolysis of the normal nitrate with boiling water. It has been used as an antacid and in combination with iodoform as a wound dressing (238). Taken internally, the subnitrate may cause fatal nitrite poisoning because of the reduction of the nitrate ion by intestinal bacteria. Bismuth subgallate, (basic bismuth gallate) [12552-60-2], dermatol, is a bright yellow powder that can be prepared by the interaction of bismuth nitrate and gallic acid in an acetic acid medium. It has been employed as a dusting powder in some skin disorders and as an ingredient of suppositories for the treatment of hemorrhoids (237,238). It has been taken orally for many years by colostomy patients in order to control fecal odors, but the drug may cause serious neurological problems (239).

BIBLIOGRAPHY

"Bismuth Compounds" in *ECT* 1st ed., Vol. 2, pp. 533–538, by R. Pasternack, Charles Pfizer & Co., Inc.; "Bismuth Preparations" in *ECT* 1st ed., Vol. 2, pp. 538–540, by G. O. Doak, U.S. Public Health Service Laboratory of Experimental Therapeutics, Johns Hopkins School of Hygiene; "Bismuth Compounds" in *ECT* 2nd ed., Vol. 3, pp. 535–549, by G. O. Doak, L. D. Freedman, and G. G. Long, North Carolina State University; "Bismuth Compounds" in *ECT* 3rd ed., Vol. 3, pp. 921–937, by G. G. Long, L. D. Freedman, and G. O. Doak, North Carolina State University; "Bismuth Compounds" in *ECT* 4th ed., Vol. 4, pp. 246–270, by G. Gilbert, Leon D. Freedman, G. O. Doak, North Carolina State University; "Bismuth Compounds" in *ECT* (online), posting date: December 4, 2000, by G. Gilbert, Leon D. Freedman, G. O. Doak, North Carolina State University.

CITED PUBLICATIONS

1. H. Onishi, *Photometric determination of traces of Metals, Part IIA: Individual Metals, Aluminium to Lithium*, 4th ed. John Wiley, and Sons, Inc., New York.
2. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, *Applied Inorganic Analysis*, 2nd ed. John Wiley, and Sons, Inc., New York, 1953.
3. G. H. Jeffery, J. Bassett, J. Mendham, and R. C. Denney, *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed., Longman Scientific and Technical, Harlow, Essex, 1989.
4. E. Upor, M. Mohai, and G. Y. Novák in G. Svehla, ed., *Wilson and Wilson's Comprehensive Analytical Chemistry*, Vol. XX, Elsevier, Amsterdam, The Netherlands, 1985, pp. 164–167.
5. H. Onishi in *Chemistry of Arsenic, Antimony and Bismuth*, N. C. Norman ed. Blackie Academic and Professional, Thomson Science, London 1998.
6. E. Amberger, *Chem. Ber.* **94**, 1447 (1961).
7. F. Paneth and co-workers, *Ber. Deut. Chem. Ges.* **51**, 1704, 1728 (1918); **55**, 769 (1922); **58**, 1138 (1925).
8. D. Cubicciotti, *J. Phys. Chem.* **64**, 791, 1506 (1966); **65**, 521 (1961).
9. J. D. Corbett and co-workers, *J. Phys. Chem.* **62**, 1149 (1958); *J. Am. Chem. Soc.* **80**, 4757 (1958); *J. Chem. Phys.* **36**, 551 (1962); *Inorg. Chem.* **2**, 979 (1963).
10. H. von Benda, A. Simon, and W. Bauhofer, *Z. Anorg. Allg. Chem.* **438**, 53 (1978).
11. H. G. von Schnering, H. von Benda, and C. Kalveram, *Z. Anorg. Allg. Chem.* **438**, 37 (1978).
12. D. Cubicciotti, *J. Electrochem. Soc.* **115**, 1138 (1968).
13. D. D. Wagman and co-workers, *Natl. Bur. Stand. Tech. Note 270-3*, U.S. Department of Commerce, Government Printing Office, Washington, D.C., 1968.
14. D. Cubicciotti, *J. Phys. Chem.* **70**, 2410 (1966).
15. D. Cubicciotti, *J. Phys. Chem.* **71**, 3066 (1967).
16. D. Cubicciotti, *Inorg. Chem.* **7**, 208 (1968).
17. D. Cubicciotti and H. Eding, *J. Phys. Chem.* **69**, 3621 (1965).
18. D. Cubicciotti, *Inorg. Chem.* **7**, 211 (1968).

19. K. Cheetham and N. Norman, *Acta Chem. Scand. Ser. A* **28A**, 55 (1974).
20. S. C. Nyburg, G. A. Ozin, and J. T. Szymanski, *Acta Crystallogr.* **B27**, 2298 (1971); **B28**, 2885 (1972).
21. P. G. Jones, D. Henschel, and A. Blaschette, *Z. Anorg. Allg. Chem.* **620**, 1037 (1994).
22. J. R. Eveland and K. H. Whitmire, *Inorg. Chim. Acta*, **249**, 41 (1996).
23. G. A. Bowmaker, F. M. M. Hannaway, P. C. Junk, A. M. Lee, B. W. Skelton, and A. H. White, *Aust. J. Chem.* **51**, 325 (1998); *Aust. J. Chem.* **51**, 331 (1998).
24. G. R. Wiley, L. T. Daly, and M. G. B. Drew. *J. Chem. Soc. Dalton Trans.* 1063 (1996).
25. R. D. Rogers, A. H. Bond, S. Aguinaga, and A. Reyes, *J. Am. Chem. Soc.* **114**, 2967 (1992).
26. C. Silvestru, H. J. Breunig, and H. Althaus, *Chem. Rev.* **99**, 3277 (1999).
27. G. A. Fisher and N. C. Norman, *Adv. Inorg. Chem.* **41**, 233 (1994).
28. H. von Benda, *Z. Kristallogr.* **151**, 271 (1980).
29. W. Clegg, M. R. J. Elsegood, V. Graham, N. C. Norman, N. L. Pickett, and K. Tavakkoli, *J. Chem. Soc. Dalton Trans.* 1743 (1994).
30. C. J. Carmalt, W. Clegg, M. R. J. Elsegood, R. J. Errington, J. Avelock, P. Lightfoot, N. C. Norman, and A. J. Scott, *Inorg. Chem.* **35**, 3709 (1996).
31. J. Beech, P. J. Cragg, and M. G. B. Drew, *J. Chem. Soc. Dalton Trans.* 719 (1994).
32. M. Ruck, *Z. Kristallogr.* **210**, 650 (1995).
33. W. Clegg, L. J. Farrugia, A. Mc Camley, N. C. Norman, A. G. Orpen, N. L. Pickett, and S. E. Stratford, *J. Chem. Soc. Dalton Trans.* 2579 (1993).
34. M. J. Vasile, G. R. Jones, and W. E. Falconer, *Adv. Mass Spectrom.* **6**, 557 (1974).
35. A. Preussman and S. Ivankovic, *Food Cosmet. Toxicol.* **13**, 543 (1975).
36. G. Malmros, *Acta Chem. Scand.* **24**, 384 (1970).
37. N. Ichinose and H. Maiwa, *Bull. Bismuth Inst.* **58**, 1 (1989).
38. I. J. Polmear, in *Chemistry of Arsenic, Antimony, and Bismuth*, N. C. Norman, ed. Blackie Academic and Professional, London 1998, p. 60.
39. H. Maeda, Y. Tanaka, M. Fukutorni, and T. Asano, *Jpn. J. Appl. Phys.* **27**, L 209 (1988).
40. K. Mariolacos, *Acta Crystallogr.* **B32**, 1947 (1976).
41. G. Gattow and G. Kiel, *Naturwissenschaften* **54**, 18 (1967); **55**, 389 (1968).
42. W. J. Ewans, J. H. Hain, Jr., and J. W. Ziller, *J. Chem. Soc. Chem. Commun.* 1628 (1989).
43. M. A. Matchett, M. Y. Chiang, and W. E. Buhro, *Inorg. Chem.* **29**, 358 (1990).
44. C. M. Jones, M. D. Burkart, and K. H. Whitmire, *Angew. Chem. Int. Ed. Engl.* **31**, 451 (1992).
45. D. A. Atwood, A. H. Cowley, R. D. Hernandez, R. A. Jones, L. L. Rand, S. G. Bott, and J. L. Atwood, *Inorg. Chem.* **32**, 2972 (1993).
46. Y. Akamine, T. Fukami, R. Nukada, M. Mikuriya, S. Deguchi, and Y. Yokota, *Bull. Chem. Soc. Jpn.* **70**, 639 (1997).
47. L. Agocs, G. G. Briand, N. Burford, T. S. Cameron, W. Kwiatkowski, and K. N. Robertson, *Inorg. Chem.* **36**, 2855 (1997).
48. W. Bensch, E. Blazso, and H. R. Oswald, *Acta Crystallogr* **C43**, 1699 (1987).
49. P. Kiprof, W. Scherer, L. Pajdla, E. Herdtweck, and W. A. Herrmann, *Chem. Ber.* **125**, 43 (1992).
50. S. I. Troyanov and A. P. Pisarevsky, *J. Chem. Soc. Chem. Commun.* 335 (1993).
51. L. K. Thompson, *Inorg. Chim. Acta*, **250**, 163 (1996).
52. M. J. Begley, D. B. Sowerby, and I. Haiduc, *J. Chem. Soc. Dalton Trans.* 145 (1987).
53. A. M. Hounslow, S. F. Lincoln, and E. R. T. Tiekink, *J. Chem. Soc. Dalton Trans.* 233, (1989).
54. K. H. Whitmire, *Adv. Organometal. Chem.* **42**, 1 (1998).

55. M. N. Bochkarev, G. A. Razuvaev, L. N. Zhakarov, and Y. T. Struchkov, *J. Organometal. Chem.* **199**, 205 (1980).
56. G. M. Kolleger, H. Siegl, K. Hassler, and K. Gruber, *Organometallics*, **15**, 4337 (1996).
57. S. Samaan, *Methoden der Organischen Chemie. Metallorganische Verbindungen As, Sb, Bi, Band XIII, Teil 8*, Georg Thieme Verlag, Stuttgart, Germany, 1978.
58. M. Wieber, *Gmelin Handbuch der Anorganischen Chemie, Band 47, Bismut-Organische Verbindungen*, Springer-Verlag, Berlin, 1977.
59. L. D. Freedman and G. O. Doak, *Chem. Rev.* **82**, 15 (1982).
60. G. O. Doak and L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony, and Bismuth*, Wiley-Interscience, New York, 1970.
61. H. Suzuki and Y. Matano eds., *Organobismuth Chemistry*, Elsevier, Amsterdam, 2001.
62. H. Suzuki and Y. Matano in *Chemistry of Arsenic, Antimony, and Bismuth*, N. C. Norman, ed. Blackie Academic and Professional, London, 1998, p. 283.
63. S. Patai, ed., *The Chemistry of organic arsenic, antimony and bismuth compounds*, John Wiley & Sons, Inc., Chichester, UK, 1994.
64. L. D. Freedman and G. O. Doak, in F. R. Hartley, ed., *The Chemistry of the Metal–Carbon Bond*, Vol. 5, John Wiley & Sons, Inc., Chichester, UK, 1989, Chapt. 9.
65. E. Wiberg and K. Mödritzer, *Z. Naturforsch., Teil B* **12B**, 132 (1957).
66. N. J. Hardman, B. Twamley, and P. P. Power, *Angew. Chem. Int. Ed. Engl.* **39**, 2771 (2000).
67. A. Banfi, M. Bartoletti, E. Bellora, and co-workers, *Synthesis* 775, (1994).
68. W. Levason, B. Sheikh, and F. P. McCullough, *J. Coord. Chem.* **12**, 53 (1982).
69. P. Bras, A. Van der Gen, and J. Wolters, *J. Organomet. Chem.* **256**, C1 (1983).
70. W. Levason, C. A. McAuliffe, and R. D. Sedgwick, *J. Organomet. Chem.* **122**, 351 (1976).
71. V. V. Sharutin and A. E. Ermoshkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 187 (1987).
72. P. J. Fagan and W. A. Nugent, *J. Am. Chem. Soc.* **110**, 2310 (1988).
73. R. S. Dickson and B. O. West, *Aust. J. Chem.* **15**, 710 (1962).
74. D. Naumann and W. Tyrra, *J. Organomet. Chem.* **334**, 323 (1987).
75. F. Challenger and C. F. Allpress, *J. Chem. Soc.* **119**, 913 (1921).
76. E. O. Fischer and S. Schreiner, *Chem. Ber.* **93**, 1417 (1960).
77. A. Marquardt, *Ber. Deut. Chem. Ges.* **20**, 1516 (1887).
78. A. Marquardt, *Ber. Deut. Chem. Ges.* **21**, 2035 (1888).
79. A. N. Nesmeyanov, V. A. Sazonova, and N. N. Sedova, *Dokl. Akad. Nauk SSSR* **198**, 590 (1971).
80. R. Müller and C. Datke, *Chem. Ber.* **99**, 1609 (1966).
81. R. E. Humphries, N. A. A. Al-Jabar, D. Bowen, A. G. Massey, and G. B. Deacon, *J. Organometal. Chem.* **319**, 59 (1987).
82. M. Wieber and K. Rudolph, *Z. Naturforsch., Teil B* **43B**, 739 (1988).
83. T. J. Juhlke, R. W. Braun, T. R. Bierschenk, and R. J. Lagow, *J. Am. Chem. Soc.* **101**, 3229 (1979).
84. T. N. Bell, B. J. Pullman, and B. O. West, *Aust. J. Chem.* **16**, 636 (1963).
85. H. Gilman and J. F. Nelson, *J. Am. Chem. Soc.* **59**, 935 (1937).
86. J. F. Nelson, *Iowa State Coll. J. Sci.* **12**, 145 (1937).
87. W. Tyrra and D. Naumann, *Can. J. Chem.* **67**, 1949 (1989).
88. A. Classen and G. Strauch, *Z. Anorg. Allg. Chem.* **141**, 82 (1924).
89. I. Ruppert and V. Bastian, *Angew. Chem. Int. Ed. Engl.* **17**, 214 (1978).
90. G. Bähr and G. Zoche, *Chem. Ber.* **90**, 1176 (1957).
91. R. A. Rossi and J. F. Bunnett, *J. Am. Chem. Soc.* **96**, 112 (1974).
92. A. J. Ashe, III, and E. G. Ludwig, Jr., *Organometallics* **1**, 1408 (1982).

93. H. J. Breunig and D. Müller, *Angew. Chem. Int. Ed. Engl.* **21**, 439 (1982).
94. A. J. Ashe, III, E. G. Ludwig, Jr., and J. Oleksyszyn, *Organometallics* **2**, 1859 (1983).
95. H. J. Breunig and D. Müller, Z. Naturforsch. *Teil B* **38B**, 125 (1983).
96. H. J. Breunig and D. Müller, *J. Organomet. Chem.* **253**, C21 (1983).
97. A. J. Ashe, III and F. J. Drone, *Organometallics* **3**, 495 (1984).
98. H. Althaus, H. J. Breunig, and E. Lork, *Organometallics* **20**, 586 (2001).
99. R. A. Brown and G. R. Dobson, *Inorg. Chim. Acta* **6**, 65 (1972).
100. A. J. Carty, N. J. Taylor, A. W. Coleman, and M. F. Lappert, *J. Chem. Soc. Chem. Commun.*, 639 (1979).
101. E. O. Fischer and K. Richter, *Chem. Ber.* **109**, 1140 (1976).
102. H. Schumann and H. J. Breunig, *J. Organomet. Chem.* **87**, 83 (1975).
103. R. A. Brown and G. R. Dobson, *J. Inorg. Nucl. Chem.* **33**, 892 (1971).
104. H. J. Breunig and U. Gräfe, *Z. Anorg. Allg. Chem.* **510**, 104 (1984).
105. J. F. White and M. F. Farona, *Inorg. Chem.* **10**, 1080 (1971).
106. W. Levason, C. A. McAuliffe, and S. G. Murray, *J. Chem. Soc. Dalton Trans.*, 711, (1977).
107. L. Vaska and J. Peone, Jr., *Suom. Kemistil., B* **44B**, 317 (1971).
108. F. Hein and H. Pobloth, *Z. Anorg. Allg. Chem.* **248**, 84 (1941).
109. H. Schumann, *Chem.-Ztg.* **110**, 121 (1986).
110. A. E. Ermoshkin, N. P. Makarenko, and K. I. Sakodynskii, *J. Chromatogr.* **290**, 377 (1984).
111. C. Barbeau, *Can. J. Chem.* **45**, 161 (1967).
112. L. W. Houk and G. R. Dobson, *Inorg. Chem.* **5**, 2119 (1966).
113. D. Benlian and M. Bigorgne, *Bull. Soc. Chim. Fr.*, 1583 (1963).
114. P. K. Baker and S. G. Fraser, *J. Coord. Chem.* **16**, 97 (1987).
115. H. Schumann, *J. Organomet. Chem.* **323**, 193 (1987).
116. P. K. Baker, S. G. Fraser, and T. M. Matthews, *Inorg. Chim. Acta* **150**, 217 (1988).
117. W. Levason, C. A. McAuliffe, and S. G. Murray, *J. Chem. Soc. Chem. Commun.*, 164 (1975).
118. G. M. Bodner, C. Gagnon, and D. N. Whittern, *J. Organomet. Chem.* **243**, 305 (1983).
119. J. Desnoyers and R. Rivest, *Can. J. Chem.* **43**, 1879 (1965).
120. E. B. Boyar and S. D. Robinson, *Inorg. Chim. Acta* **76**, L137 (1983).
121. E. B. Boyar and S. D. Robinson, *J. Chem. Soc. Dalton Trans.* 629 (1985).
122. R. H. Nutall, E. R. Roberts, and D. W. A. Sharp, *J. Chem. Soc.* 2854 (1962).
123. S. Ahrland, T. Berg, and P. Trinderup, *Acta Chem. Scand. Ser. A* **A31**, 775 (1977).
124. F. Hultén and I. Persson, *Inorg. Chim. Acta* **128**, 43 (1987).
125. J. Selbin, N. Ahmad, and M. J. Pribble, *J. Inorg. Nucl. Chem.* **32**, 3249 (1970).
126. R. Talay and D. Rehder, *Chem. Ber.* **111**, 1978 (1978).
127. J. Cassidy and K. H. Whitmire, *Inorg. Chem.* **28**, 3164 (1989); **30**, 2788 (1991).
128. A. M. Arif, A. H. Cowley, N. C. Norman, and M. Pakulski, *Inorg. Chem.* **25**, 4836 (1986).
129. C. Chen, Y. Liao, and Y.-Z. Huang, *Tetrahedron* **45**, 3011 (1989).
130. J. Zhang and co-workers, *Appl. Phys. Lett.* **54**, 1166 (1989).
131. T. Masuda and co-workers, *Macromolecules* **21**, 281 (1988).
132. F. J. Martin and K. R. Price, *J. Appl. Polym. Sci.* **12**, 143 (1968).
133. K. H. Ebert, R. E. Schulz, H. J. Breunig, C. Silvestru, and I. Haiduc, *J. Organometal. Chem.* **470**, 93 (1994).
134. R. Okawara, K. Yasuda, and M. Inoue, *Bull. Chem. Soc. Jpn.* **39**, 1823 (1966).
135. M. Wieber and I. Sauer, *Z. Naturforsch. Teil B* **42B**, 695 (1987).
136. M. Ali, S. P. Bond, S. A. Mbogo, W. R. McWhinnie, and P. M. Watts, *J. Organomet. Chem.* **371**, 11 (1989).
137. H. Gilman and H. L. Yablunky, *J. Am. Chem. Soc.* **63**, 207 (1941).

138. F. Dünhaupt, *Liebigs Ann. Chem.* **92**, 371 (1854).
139. F. F. Blicke, U. O. Oakdale, and F. D. Smith, *J. Am. Chem. Soc.* **53**, 1025 (1931).
140. F. Dünhaupt, *J. Prakt. Chem.* **61**, 399 (1854).
141. D. Hellwinkel and M. Bach, *J. Organometal. Chem.* **17**, 389 (1969).
142. A. E. Goddard, J. N. Ashley, and R. B. Evans, *J. Chem. Soc.* **121**, 978 (1922).
143. L. Maier, *Tetrahedron Lett.* **6**, 1 (1959).
144. A. J. Ashe, III, *Acc. Chem. Res.* **11**, 153 (1978).
145. N. I. Anishchenko, E. M. Panov, O. P. Syutkina, and K. A. Kocheshkov, *Zh. Obshch. Khim.* **49**, 1185 (1979).
146. G. Grüttner and M. Wiernik, *Ber. Deut. Chem. Ges.* **48**, 1473 (1915).
147. H. Althaus, H. J. Breunig, R. Rösler, and E. Lork, *Organometallics*, **18**, 328 (1999).
148. W. Tyrra and D. Naumann, *Can. J. Chem.* **67**, 1949 (1989).
149. H. Gilman and H. L. Yale, *Chem. Rev.* **30**, 281 (1942).
150. H. McCombie and B. C. Saunders, *Nature (London)* **159**, 491 (1947).
151. W. Clegg, R. J. Errington, G. A. Fisher, D. C. R. Hockless, N. C. Norman, A. G. Orpen, and S. E. Stratfort, *J. Chem. Soc. Dalton Trans.*, 1967 (1992).
152. W. Clegg, R. J. Errington, G. A. Fisher, G. A. Flynn, and N. C. Norman, *J. Chem. Soc. Dalton Trans.*, 637 (1993).
153. G. Faraglia, *J. Organomet. Chem.* **20**, 99 (1969).
154. M. Wieber and U. Baudis, *Z. Anorg. Allg. Chem.* **439**, 134 (1978).
155. F. Huber and S. Bock, *Z. Naturforsch., Teil B* **37B**, 815 (1982).
156. O. J. Scherer, P. Hornig, and M. Schmidt, *J. Organomet. Chem.* **6**, 259 (1966).
157. P. Krommes and J. Lorberth, *J. Organomet. Chem.* **93**, 339 (1975).
158. W. T. Reichle, *J. Organomet. Chem.* **13**, 529 (1968).
159. R. G. Goel and H. S. Prasad, *Spectrochim. Acta, Part A* **35A**, 339 (1979).
160. M. Wieber, D. Wirth, and K. Hess, *Z. Anorg. Allg. Chem.* **505**, 138 (1983).
161. F. Challenger and J. F. Wilkinson, *J. Chem. Soc.* **121**, 91 (1922).
162. E. J. Kupchik and C. T. Theisen, *J. Organomet. Chem.* **11**, 627 (1968).
163. M. Wieber and A. Basel, *Z. Anorg. Allg. Chem.* **448**, 89 (1979).
164. M. Wieber, I. Fetzer-Kremling, D. Wirth, and H. G. Rüdling, *Z. Anorg. Allg. Chem.* **520**, 59 (1985).
165. T. Klapötke, *J. Organomet. Chem.* **331**, 299 (1987).
166. H. Schmidbaur and M. Bergfeld, *Z. Anorg. Allg. Chem.* **363**, 84 (1968).
167. M. Wieber, H. G. Rüdling, and Ch. Burschka, *Z. Anorg. Allg. Chem.* **470**, 171 (1980).
168. D. D. Davis and C. E. Gray, *Organomet. Chem. Rev. Sect. A* **6**, 283 (1970).
169. W. Frank, *J. Organomet. Chem.* **177**, 386 (1990).
170. H. Sitzmann and G. Wolmershäuser, *Chem. Ber.* **127**, 1335 (1994).
171. H. Sitzmann and G. Wolmershäuser, *Z. Naturforsch.* **52b**, 398 (1997).
172. C. J. Carmalt, L. I. Farrugia, and N. C. Norman, *J. Chem. Soc. Dalton Trans.* 443 (1996).
173. C. J. Carmalt, D. Walsh, A. H. Cowley, and N. C. Norman, *Organometallics* **16**, 3597 (1997).
174. K. J. Akiba and co-workers, *J. Am. Chem. Soc.*, **117**, 3922 (1995); *Heteroatom. Chem.* **4**, 293 (1995).
175. A. J. Ashe, III, *Adv. Organomet. Chem.* **30**, 77 (1990).
176. F. Calderazzo, A. Morvillo, G. Pelizzi, and R. Poli, *J. Chem. Soc. Chem. Commun.*, 507 (1983).
177. A. J. Ashe, III, C. M. Kausch, and O. Eisenstein, *Organometallics* **6**, 1185 (1987).
178. F. Calderazzo, R. Poli, and G. Pelizzi, *J. Chem. Soc. Dalton Trans.*, 2365 (1984).
179. M. Wieber and I. Sauer, *Z. Naturforsch., Teil B* **39B**, 887 (1984).
180. F. Calderazzo, A. Morvill, G. Pelizzi, R. Poli, and F. Ungari, *Inorg. Chem.* **27**, 3730 (1988).

181. H. J. Breunig and D. Müller, *Z. Naturforsch., Teil B* **41B**, 1129 (1986).
182. M. Wieber and I. Sauer, *Z. Naturforsch., Teil B* **39B**, 1668 (1984).
183. O. Mundt, G. Becker, M. Rössler, and C. Witthauer, *Z. Anorg. Allg. Chem.* **506**, 42 (1983).
184. H. J. Breunig, R. Rösler, and E. Lork, *Angew. Chem. Int. Ed. Engl.* **37**, 3175 (1998).
185. H. J. Breunig and R. Rösler, *Chem. Soc. Rev.* **29**, 403 (2000).
186. N. Tokitoh, Y. Arai, S. Okazaki, and S. Nagase, *Science* **277**, 78 (1997).
187. N. Tokitoh, Y. Arai, and S. Okazaki, *Phosphorus Sulfur Silicon* **124**, 371 (1997).
188. N. Tokitoh, *J. Organomet. Chem.* **611**, 217 (2000).
189. B. Twamley, C. D. Sofield, M. M. Olmstead, and P. P. Power, *J. Am. Chem. Soc.* **121**, 3357 (1999).
190. P. P. Power, *Chem. Rev.* **99**, 3463 (1999).
191. T. Sasamori, N. Takeda, and N. Tokitoh, *Chem. Commun.* 1353 (2000).
192. W. Frank, V. Reiland, and G. J. Reiß, *Angew. Chem. Int. Ed. Engl.* **37**, 2984 (1998).
193. A. J. Ashe, III, *Top. Curr. Chem.* **105**, 125 (1982).
194. A. J. Ashe, III, T. R. Diephouse, and M. Y. El-Sheikh, *J. Am. Chem. Soc.* **104**, 5693 (1982).
195. T. Ogawa, T. Murafuji, K. Iwata, and H. Suzuki, *Chem. Lett.*, 2021 (1988).
196. T. Ogawa, T. Miyazaki, and H. Suzuki, *Chem. Lett.*, 1651 (1990).
197. S. Wallenhauer and K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **33**, 976 (1994).
198. A. E. Borisov, M. A. Osinova, and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR Ser. Khim.*, 1507 (1963).
199. P. Raj, K. Singhal, and R. Rastogi, *Polyhedron* **5**, 677 (1986).
200. R. Rüther, F. Huber, and H. Preut, *Z. Anorg. Allg. Chem.* **539**, 110 (1986).
201. D. H. R. Barton, N. Y. Bhatnagar, J.-P. Finet, and W. B. Motherwell, *Tetrahedron* **42**, 311 (1986).
202. V. A. Dodonov, A. V. Gushchin, and M. B. Ezhova, *Zh. Obshch. Khim.* **58**, 2170 (1988).
203. R. G. Goel and H. S. Prasad, *J. Organomet. Chem.* **50**, 129 (1973).
204. R. G. Goel and H. S. Prasad, *J. Organomet. Chem.* **36**, 323 (1972).
205. R. G. Goel and H. S. Prasad, *Spectrochim. Acta, Part A* **32A**, 569 (1976).
206. F. Challenger and A. E. Goddard, *J. Chem. Soc.* **117**, 762 (1930).
207. D. H. R. Barton and J.-P. Finet, *Pure Appl. Chem.* **59**, 937 (1987).
208. D. H. R. Barton, W. B. Motherwell, B. da Silva, and M. Teresa, *Rev. Port. Quim.* **26**, 177 (1984).
209. J.-P. Finet, *Chem. Rev.* **89**, 1487 (1989).
210. Fr. Demande 2,441,602 (June 13, 1980), D. Barton and W. B. Motherwell (to Agence Nationale de Valorisation de la Recherche).
211. U.S. Pat. 3,239,411 (Mar. 8, 1966), J. R. Leebrick (to M&T Chemicals, Inc.).
212. Neth. Appl. 6,405,309 (Nov. 16, 1964), (to M&T Chemicals, Inc.).
213. P. Evrard and P. Lepoivre, *Parasitica* **39**, 117 (1983).
214. Jpn. Kokai Tokkyo Koho 82 49614 (Mar. 23, 1982), (to Mitsubishi Petrochemical Co., Ltd.).
215. G. Wittig and K. Clauss, *Liebigs Ann. Chem.* **578**, 136 (1952).
216. O. A. Ptitsyna, M. E. Gurskii, T. D. Maiorova, and O. Reutov, *Izv. Akad. Nauk SSSR Ser. Khim.*, 2618 (1971).
217. R. Dötzer, *Abstracts of Papers of the 3rd International Symposium on Organometallic Chemistry*, Munich, Germany, Aug. 28–Sept. 1, 1967, p. 196.
218. R. G. Goel and H. S. Prasad, *J. Chem. Soc. A*, 562 (1971).
219. G. O. Doak, G. G. Long, S. K. Kakar, and L. D. Freedman, *J. Am. Chem. Soc.* **88**, 2342 (1966).
220. D. Lloyd and M. I. C. Singer, *J. Chem. Soc. Chem. Commun.*, 1042 (1967).

221. D. H. R. Barton and co-workers, *J. Chem. Soc. Perkin Trans.* **1**, 2667 (1985).
222. H. Suzuki, T. Murafuji, and T. Ogawa, *Chem. Lett.*, 847 (1988).
223. T. Ogawa, T. Murafuji, and H. Suzuki, *Chem. Lett.*, 849 (1988).
224. C. Glidewell, D. Lloyd, and S. Metcalfe, *Synthesis*, 319 (1988).
225. G. Wittig and D. Hellwinkel, *Chem. Ber.* **97**, 789 (1964).
226. A. Schmuck, J. Buschmann, J. Fuchs, and K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **26**, 1180 (1987).
227. A. Schmuck and K. Seppelt, *Chem. Ber.* **122**, 803 (1989).
228. C. Levaditi, *Lancet* **204**, 639 (1923).
229. J. E. Moore, *The Modern Treatment of Syphilis*, 2nd ed., Charles C. Thomas, Springfield, Ill., 1941, pp. 134–153.
230. F. N. Judson, in Y. M. Felman, ed., *Sexually Transmitted Diseases*, Churchill Livingstone, New York, 1986, pp. 23–37.
231. N. J. Fiumara, in Ref. 230, pp. 39–50.
232. Th. Klapötke, *Biol. Met.* **1**, 69 (1988).
233. L. L. Brunton, in A. G. Gilman, T. W. Rall, A. S. Niews, and P. Taylor, eds., *Goodman and Gilman's The Pharmacological Basis of Therapeutics*, 8th ed., Pergamon Press, New York, 1990, pp. 910, 911.
234. J. Reglinsky in *Chemistry of Arsenic, Antimony and Bismuth*, N. C. Norman, ed. Blackie Academic and Professional, Thomson Science; London, 1998.
235. U. Wormser and I. Nir in *The Chemistry of Organic Arsenic, Antimony, and Bismuth Compounds*, S. Patai ed., J. Wiley & Sons, Inc., Chichester, 1994.
236. G. G. Briand and N. Burford, *Chem. Rev.* **99**, 2601 (1999).
237. *Drug Evaluations*, 6th ed., American Medical Association Department of Drugs, W. B. Saunders Company, Philadelphia, Pa., 1986, p. 1568.
238. J. E. F. Reynolds, ed., Martindale. *The Extra Pharmacopoeia*, 29th ed., The Pharmaceutical Press, London, 1989, p. 1548.
239. F. P. Morgan and J. J. Billings, *Med. J. Aust.* (2), 662 (1974).

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