# BISMUTH

## ANNUAL SURVEY COVERING THE YEAR 1972

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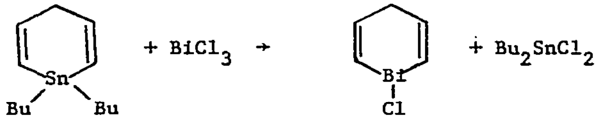
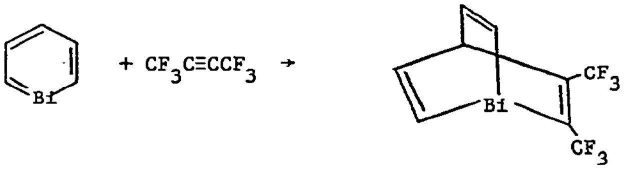
A comprehensive survey of the information on organoarsenic, -antimony, and -bismuth chemistry published between 1965 and 1968 has appeared as a supplement [1] to Dub's *Compounds of Arsenic, Antimony, and Bismuth, 1937-1964*, while Crow and Cullen [2] have written a critical review of recent work on organic compounds of the three elements. Organobismuth compounds have been briefly mentioned in review articles on the synthesis of organometallic compounds via aryldiazonium and diarylhalonium salts [3,4], organotin compounds containing Sn-P, Sn-As, Sn-Sb, or Sn-Bi bonds [5], free radical reactions of organometallic compounds [6], the application of the Grignard reaction to the preparation of organometallic compounds [7], and the thermal decomposition of metal alkyls [8].

The synthesis of bismabenzene(bismin) has been attempted by Ashe and Gordon [9]. (In 1971 Ashe succeeded in preparing phospha-, arsa-, and stibabenzene.) The first step in the attempted synthesis of bismabenzene involved the formation of a heterocyclic chlorobismuthine:



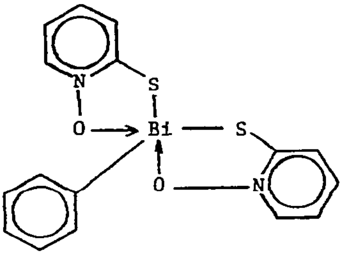
This compound was obtained in 75% yield as yellow crystals melting at 144-145° with decomposition. Treatment of a THF solution of the chlorobismuthine with 1,5-diazabicyclo[4.3.0]non-5-ene(DBN) resulted in an exothermic loss of hydrogen chloride, but bismabenzene could not be isolated from the reaction mixture. A 1:1 adduct of bismabenzene and hexafluoro-2-butyne could be obtained, however, by addition of the latter compound to the THF solution after precipitation of the DBN hydrochloride. The adduct was shown to be a bicyclic compound, presumably formed by a Diels-Alder type of reaction:



Although pyridine does not undergo Diels-Alder reactions, Ashe found that the other group V heteroaromatics did give bicyclic 1:1 adducts. Phosphabenzene reacted slowly with hexafluoro-2-butyne at 100°, while arsabenzene formed the adduct at room temperature. Stibabenzene reacted rapidly even at 0°. It was concluded that the resonance energy of the group V heteroaromatics decreased as the atomic number of the hetero atom increased.

The reaction of phenyldihalobismuthines with 1,10-phenanthroline(Phen) or 2,2'-bipyridine(Bipy) has been found to yield adducts of the type $PhBiX_2 \cdot L$, where X was Cl, Br, or I and L was Phen or Bipy [10]. Attempts to prepare adducts of diphenylhalobismuthines and these ligands were, however, unsuccessful. Molecular weight determinations showed that the phenyldihalobismuthine complexes were monomeric in dichloromethane, and conductivity measurements indicated that the complexes were only slightly dissociated in nitromethane. The electronic spectrum of uncomplexed phenyldibromobismuthine in dichloromethane exhibited a maximum at 341nm. In the solid state the maximum shifted to higher wavelengths; this result was attributed to the formation of bromine bridges and weakening of the Bi-Br bond. The absorption bands of the adducts in the solid state and in dichloromethane occurred at lower wavelengths than those found for phenyldibromobismuthine under the same conditions. The spectra of the phenyldiiodobismuthine adducts showed similar behavior. The electronic spectra appeared to confirm the conclusion that the adducts did not decompose to the starting compounds in solution and that complex formation led to breaking of the bismuth-halogen bridges existing in the uncomplexed phenyldihalobismuthines. The IR spectra of the adducts were consistent with the presence of coordinated Bipy and Phen. It was concluded that the adducts contained pentacoordinated bismuth and that Bipy and Phen were acting as bidentate (and presumably chelating) ligands.

Curry and Jandacek [11] have synthesized and determined the crystal structure of bis(1-oxopyridine-2-thiolato)phenylbismuthine:



The compound was prepared by the interaction of sodium 1-oxopyridine-2-thiolate and either phenyldiiodobismuthine or diphenylacetatobismuthine. The coordination about the bismuth atom was found to be approximately octahedral with a pair of electrons presumably occupying one coordination site. The bismuth atom and the sulfur and oxygen atoms were almost exactly in the same plane. The plane of the phenyl group was nearly perpendicular to this plane. The C-Bi bond distance was 2.26(2)Å, not significantly different from the corresponding distance in triphenylbismuthine.

In 1969 Royo and Uson [12] prepared tris(pentafluorophenyl)bismuthine by the Grignard reaction and noted that the compound decomposed readily in the presence of water to give bismuth hydroxide and pentafluorobenzene. The abstract of their article in *Chem. Abstr.*, 75 (1971) 76963k, erroneously stated, however, that decafluorobiphenyl and bismuth metal were formed in the hydrolysis. Since only this abstract was available to the present authors, we repeated this error in our annual survey of organobismuth chemistry for 1971 [13]. Deacon and Johnson [14] were also misled by the abstract when they reinvestigated the properties of tris(pentafluorophenyl)bismuthine. They reported that the compound showed reasonable thermal stability but was hydrolyzed at room temperature to give bismuth hydroxide and pentafluorobenzene:

$$(C_6F_5)_3Bi + 3H_2O \rightarrow Bi(OH)_3 + 3C_6F_5H$$

They also found that tris(pentafluorophenyl)bismuthine underwent transmetallation reactions with a number of representative elements:

$$n(C_6F_5)_3Bi + 3M \rightarrow 3(C_6F_5)_nM + nBi$$

(where M was Hg, In, Sn, As, or S)

In a later note Deacon and Johnson [15] pointed out that they had become aware of the error in *Chem. Abstr.* and that their results concerning the hydrolysis were in agreement with those of Royo and Uson. And, finally, *Chem. Abstr.*, 77 (1972) 101807p, published a correction of their earlier abstract.

Deacon and Fallon [16] have studied the preparation of triarylbismuthines by the thermal decomposition of tris(arenesulfinato)bismuthines at about 200°:

$$Bi(O_2SAr)_3 \rightarrow 3SO_2 + Ar_3Bi$$

(where Ar was Ph, $p$-Me$C_6H_4$, or $p$-Cl$C_6H_4$)

The yields ranged from 40-80% in these cases. Pyrolysis of two other tris-

(arenesulfinato)bismuthines (where Ar was 2,4,6-$(Me_2CH)_3C_6H_2$ or *p*-$MeCONHC_6H_4$) did not, however, give organobismuth compounds.

Kyuntsel and Shishkin [17] have measured the $^{209}Bi$, $^{35}Cl$, and $^{79}Br$ NQR spectra of tris(p-chlorophenyl)- and tris(*p*-bromophenyl)bismuthine at 77°K and observed the frequencies corresponding to all the bismuth, chlorine, and bromine transitions. It was concluded that all the triarylbismuthine molecules in a given compound were equivalent; *i.e.*, their electronic environments were identical. Within each molecule, however, the substituent atoms (*i.e.*, chlorine or bromine) had different electronic environments. These differences may have arisen from different degrees of π-conjugation between the central bismuth atom and the three aryl groups to which it was attached.

There have been a few other recent investigations of the spectral properties of tertiary bismuthines. Thus, Petrov and coworkers [18] have studied the effect of various types of substituents on the PMR spectra of triarylbismuthines. In addition, papers discussed under Arsenic have included information on the mass spectra of trialkylbismuthines [19,20] and on the use of quantum mechanics for correlating the chemical and optical properties of triphenylphosphine, -arsine, -stibine, and -bismuthine [21].

Brown and Dobson [22] have included $Ph_3BiCr(CO)_5$, $Ph_3BiMo(CO)_5$, and $Ph_3BiW(CO)_5$ in a study of the IR spectra of thirty-seven octahedral complexes of the type $LM(CO)_5$, where M was Cr, Mo, or W and L was a Lewis base bonded through a N, P, As, Sb, Bi, O or S donor atom. It was found that the position of the M-C stretching absorption (E-mode) was determined by the identity of the donor atom and was lowest for the "hard" bases. Within a series of complexes containing the same donor atom, there was a reciprocal relationship between the M-C and C-O stretching frequencies. The triphenylbismuthine derivatives in solution were unstable to oxygen and required rigorous exclusion of air to prevent decomposition.

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Organobismuth compounds have been mentioned in the recent patent literature. Thus, a German patent [23] has claimed that triphenylbismuthine was a catalyst for the condensation of azelaic acid and bis(*p*-aminophenyl) sulfone to a polyamide copolymer. Triphenylbismuthine has also been said to be useful in preparing corona-resistant electrical insulation [24], and organobismuth derivatives of pyrimidinethiols have been reported to have fungicidal activity [25]. The use of triarylbismuthines as synergists for phenolic antioxidants in polyethylene and polypropylene has been described in a Japanese patent [26].

Dahlmann and Winsel [27] have reported in an East German patent that tertiary bismuthines reacted with haloimides to form imido bismuthonium halides:

$$R_3Bi + R'_2NX \rightarrow [R_3BiNR'_2]X$$

(where R was Me or Ph, $R'_2NH$ was succinimide or phthalimide, and X was Cl or Br)

In a second patent the authors [28] described the formation of triphenyl-(8-quinolinyloxy)bismuthonium bromide by displacement of the imido group from the corresponding imido bismuthonium salt. Both of these patents have been discussed in more detail under Antimony. The chemical and spectral properties of triphenylbismuthonium tetraphenylcyclopentadienylide [29] have also been discussed in the Antimony section.

Keck and Klar [30] have described the preparation of tris(*p*-dimethylaminophenyl)bismuth dichloride by means of the following reaction:

$$(p\text{-}Me_2NC_6H_4)_3Bi + PhICl_2 \rightarrow (p\text{-}Me_2NC_6H_4)_3BiCl_2 + PhI$$

The UV and PMR spectra of this compound were determined and compared with those of similar compounds of phosphorus, arsenic, and antimony. These results have been discussed under Antimony. In a second paper the same authors [31] indicated that the bismuth dichloride reacted with antimony pentachloride or aluminum chloride to form salts of the type $[Ar_3Bi][SbCl_6]_2$ or $[Ar_3Bi][AlCl_4]_2$. They were, however, unable to purify these substances. This work has also been mentioned under Antimony.

Faraglia and coworkers [32] have investigated the preparation and structure of the organobismuth(V) derivatives $Ph_3BiCl(Ox)$ and $Ph_3BiBr(Ox)$, where Ox was the oxinate (8-quinolinolate) group. The compounds were obtained by mixing equimolar amounts of triphenylbismuth dihalide in methylene dichloride or chloroform and sodium oxinate in absolute ethanol. Osmometry in benzene and conductivity measurements in methanol showed that the organobismuth oxinates existed in solution as essentially monomeric undissociated species. The electronic spectra of the complexes in the solid state exhibited absorption bands centered around 360 nm, which were considered characteristic of a chelating oxinate group. The IR spectra were consistent with this interpretation and also suggested the presence of bismuth-halogen bonds. It was concluded that the solid complexes contained bismuth atoms coordinated to the oxygen and nitrogen atoms of the oxinate ligand and to the halogen atom; *i.e.*, the bismuth was hexacoordinate and presumably octahedral. Evidence was also presented that indicated that the bismuth-nitrogen bonds were weakened in solution and tended to undergo cleavage.

Goel and Prasad [33] have prepared and studied the structures of six oxybis(triphenylbismuth) derivatives of the type $(Ph_3BiOBiPh_3)X_2$, where X was $ClO_4$, $NO_3$, Cl, Br, NCO, or $CF_3CO_2$. A dihydrate of the diperchlorate was obtained by the reaction of a benzene solution of triphenylbismuth dichloride with an aqueous solution of silver perchlorate. The anhydrous diperchlorate could be obtained by drying the dihydrate *in vacuo* for about a week or by recrystallizing the dihydrate from aqueous ethanol. Oxybis(triphenylbismuth) dinitrate was prepared by the reaction of an acetone solution of triphenylbismuth dichloride with an aqueous solution of silver nitrate. The reaction between equimolar amounts of triphenylbismuth dichloride or dibromide and alcoholic sodium or potassium hydroxide gave oxybis(triphenylbismuth) dichloride or dibromide. Oxybis(triphenylbismuth) dicyanate and bis(trifluoroacetate) were obtained by the metathetical reactions of oxybis(triphenylbismuth) dichloride with silver cyanate and silver trifluoroacetate, respectively. In a number of cases, the expected oxybis(triphenylbismuth) compounds were not obtained. Thus, the main product of the interaction of triphenylbismuth dichloride and silver tetrafluoroborate was triphenylbismuth difluoride. The reaction of triphenylbismuth dichloride with silver cyanate and trifluoroacetate gave triphenylbismuth dicyanate and bis(trifluoroacetate), respectively. Treatment of triphenylbismuth difluoride with alkali hydroxide yielded triphenylbismuthine. An attempted metathetical reaction of oxybis(triphenylbismuth) dichloride with silver acetate also gave mainly triphenylbismuthine.

The IR spectrum of the dihydrate of oxybis(triphenylbismuth) diperchlorate suggested that this compound had an ionic structure containing the hydrated cation $[Ph_3Bi(H_2O)]_2O^{2+}$. The IR spectra of the other oxybis derivatives indicated that they were non-ionic compounds in the solid state and that the anionic groups acted as monodentate ligands. Conductance measurements showed that both hydrated and anhydrous diperchlorates behaved as 1:2 electrolytes in acetonitrile but that the other compounds were not significantly ionized. In dichloromethane even the diperchlorate (whether hydrated or anhydrous) appeared to be un-ionized.

Goel and Prasad have also succeeded in obtaining triphenylbismuthine oxide, $Ph_3BiO$, by treatment of a benzene solution of triphenylbismuth dichloride with silver oxide. The IR spectrum of triphenylbismuthine oxide exhibited a strong band at $625 cm^{-1}$ attributed to the Bi-O-Bi asymmetric stretch. Similar bands were observed in the spectra of the oxybis compounds. It was suggested that the oxide had a five coordinate polymeric structure involving -Bi-O-Bi- units. The low solubility of this compound in organic solvents was consistent with this formulation.

Beaumont and Goel [34] have converted tetraphenylbismuth chloride by means of metathetical reactions to the corresponding nitrate and trichloroacetate. Unlike the chloride, which decomposed in a few minutes at room temperature, both the nitrate and trichloroacetate were stable at room temperature for at least a few hours. THe IR spectra of the latter two compounds indicated that the anionic groups were present as monodentate ligands. The molecular weights in benzene were normal and hence confirmed the molecular constitution of the nitrate and trichloroacetate. Conductance measurements in nitromethane or in acetonitrile showed that the trichloroacetate was also non-ionic in these solvents; the nitrate, however, was ionized under these conditions.

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